

Synthesis of minerals

Kovalev V.N.¹, Setkova T. V.², Balitsky V. S,
²Kalinin G.M.², Borovikova E.Y.¹ **Growth of
 α -Si_{1-x}Ge_xO₂ solid solution single crystals in
boric acid hydrothermal solutions.** UDC:
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Abstract. We report new experimental data on α -Si_{1-x}Ge_xO₂ crystal growth in boric acid hydrothermal solutions. Crystal growth was carried out by hydrothermal temperature-difference method in autoclaves in the temperature range of 450–650°C and pressure of 100 MPa. A significant influence of temperature on crystal growth rate and incorporation of germanium impurity into grown crystals has been determined. The GeO₂ content in the (c) growth sectors varies from 13.2 wt.% at 400/450°C to 19.2 wt.% at 600/650°C, which is ~20% higher than in crystals grown in fluoride solutions under similar PT-conditions. The distribution of germanium over the overgrown layer is uniform, the differences in the impurity content in growth sectors do not exceed 2-3 wt.%. The maximum crystal growth rate at 600/650°C along the pinacoid (0001) growth direction $V_{(0001)}$ is 0.04 mm/day, which is 20% less than of crystals grown in fluoride solutions under the similar PT-conditions.

Keywords: hydrothermal quartz crystals growth; germanium; single crystals; piezoelectric materials; boric acid

Quartz single crystals are an important piezoelectric material that has been being studied and used in many industries for more than 80 years. Except quartz, there group of compounds with α -quartz-like structure and, consequently, piezoelectric properties. These include α -GeO₂ and compounds of the AXO₄-type (A = Al, Ga, Fe, X = P, As) (Philippot et al., 1996). These materials have higher values of piezoelectric constants in comparison with a pure quartz, but their synthesis on an industrial scale is a complex process and economically unprofitable. Significant progress has been made in the hydrothermal growth of α -Si_{1-x}Ge_xO₂ solid solution single crystals. These crystals are characterized by superior piezoelectric properties to the compounds mentioned above. Fluoride hydrothermal solutions (Balitsky et al., 2004; Balitsky et al., 2009; Ranieri et al., 2011) demonstrated the greatest efficiency in α -Si_{1-x}Ge_xO₂ synthesis. Fluorine in aqueous hydrothermal solutions contributes to a more intensive dissolution of quartz and germanium dioxide. In this case, hydrofluoride complexes of germanium and silicon of the A(OH)_{4-y}F_y (A = Si, Ge; y - integer) type are formed. Recent research demonstrates (Balitsky et

al., 2017) that high-germanium quartz single crystals (germania content < 15 wt.%) can be obtained using fluoride hydrothermal solutions under high temperatures and pressures.

However, several problems may arise due to using fluoride solutions. The first one is high PT-conditions that may be used in laboratory synthesis. However, these conditions cannot be applied to industrial techniques. The second problem is heterogeneity of germanium distribution over the overgrowth layer and the formation of twins (Balitsky et al., 2009). To solve these problems, hydrothermal method of α -Si_{1-x}Ge_xO₂ crystals growth should be modified.

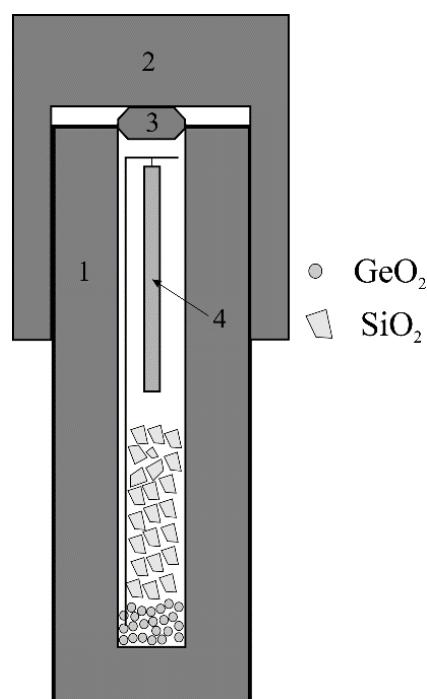


Fig.1 Scheme of loading the autoclave for the experiment. Designations: 1 – autoclave body, 2 – autoclave lid, 3 – obturator, 4 – seed

We have carried out research on modifying the method of α -Si_{1-x}Ge_xO₂ solid solution crystals synthesis by changing the composition of the hydrothermal solution. As a mineralizer, boric acid solution (30 wt.% H₃BO₃) was taken. Boron in hydrothermal solutions increases the solubility of silica in comparison to the pure aqueous fluid. First experiments on silica dissolution in boron-rich systems were carried out by Pichavant. The increase of silica dissolution with an increase of boron concentration in solutions was reported (Pichavant, 1983). Later the temperature dependence of silica solubility in boric acid hydrothermal solutions in a wide boric acid concentration range was determined (Balitsky et al., 1998). In our work hydrothermal experiments were carried out in autoclaves in a wide

temperature range: $T_1/T_2 = 400/450^\circ, 500/550^\circ, 600/650^\circ$, where T_1 and T_2 are the temperature in the upper and lower parts of the autoclave respectively. The temperature difference between the dissolution and crystallization zones is 50° . The pressure during the experiment was estimated by the autoclave filling coefficient and was 100 MPa. The charge was a mixture of reagent α - GeO_2 and fragments of natural quartz in a ratio of 1:25. The seed was a single crystal quartz rod, which was fixed on a metal frame in the upper part of the crystallization zone. The autoclave loading is shown in Fig.1.

From grown crystals polished plates were made, the surface of last ones were coated. The study of polished plates was carried out on a scanning

electron microscope Tescan Vega II XMU (Tescan, Czech Republic), equipped with an INCA Energy 450 X-ray spectral microanalysis system with energy dispersive (INCA Xsight) and crystal diffraction (INCA Wave 700) X-ray spectrometers (Oxford Instruments, England) and the INCA Energy+ software platform. SiO_2 (Si-K $_{\alpha}$) and germanium metal (Ge-L $_{\alpha}$) were used as standards for the elements. Electronic images of polished plates are shown in Fig.2.

By the formation of an overgrown layer on the seed, we can conclude that the temperature coefficient of solubility of the charge components in boric acid solutions under experiments conditions is positive.

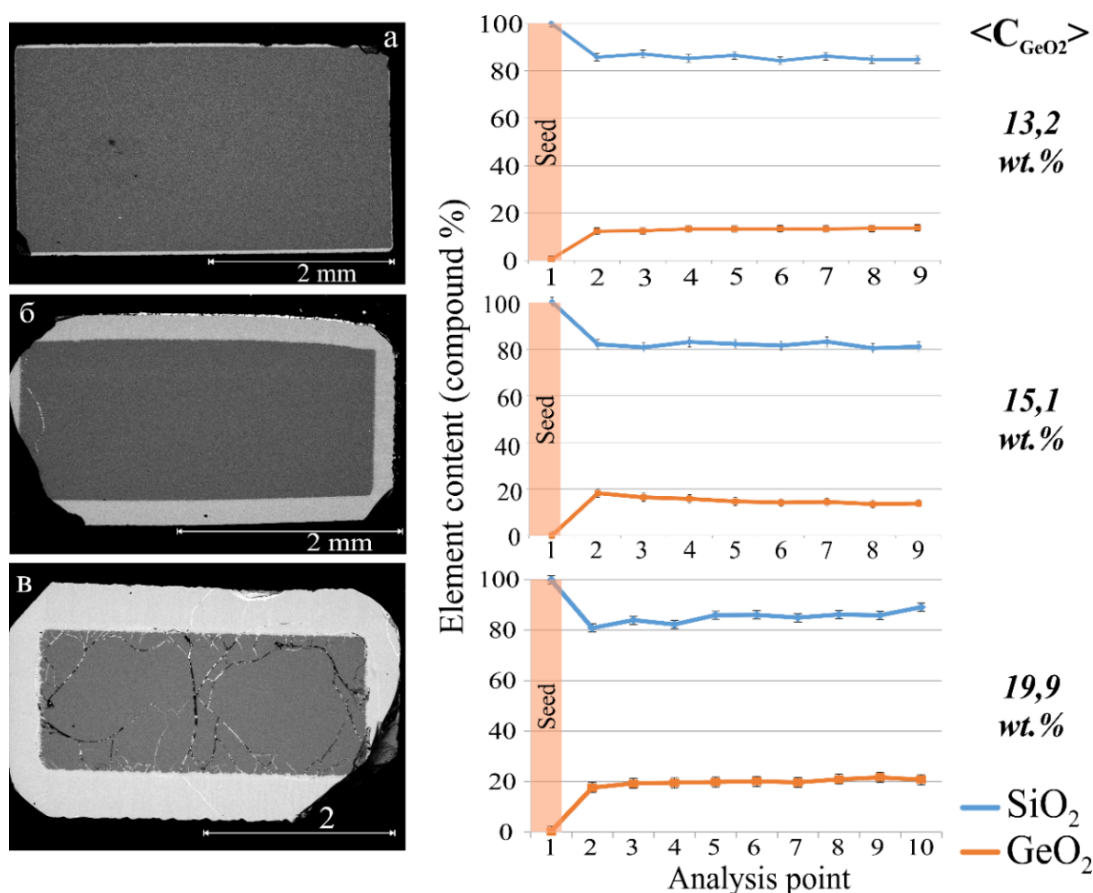


Fig.2 SEM-images of polished crystal plates grown at a) 400/450°C, b) 500/550°C and c) 600/650°C. On the right are graphs of the impurity distribution over the overgrown layer in the pinakoid growth sector. Average concentration of germanium in the pinakoid growth sectors is indicated.

It can be assumed that the transfer of components is carried out in the form of complex heteropoly acids of the $(\text{H}_3\text{BO}_3)_n(\text{H}_4\text{AO}_4)_m$ (A = Si, Ge) type. This assumption is based on the existence of a whole group of borosilicate minerals formed in nature under conditions close to experimental ones (Godovikov, 1983). The determination of the stoichiometry of the complex (the ratio of silicon and boron in it) under synthesis conditions is separate research.

The role of borate ions in the silica and germania transfer is actively discussed. Some studies provide

data on silicon transfer in viscous silicon liquids in the form of polyborate complexes, able to concentrate many elements, in our case, germanium (Peretyazhko et al., 2010).

The temperature of the experiment significantly affects the incorporation of germanium impurity into the overgrown layer. The average GeO_2 content in the growth sectors of the $\langle c \rangle$ face varies from 13.2 wt.% at 400/450°C to 19.2 wt.% at 600/650°C. These concentrations are ~20% higher than when using fluoride solutions at these temperatures. Also, the use

of boric acid solutions contributes to the formation of a more homogeneous overgrown layer: the difference in germanium concentration in growth sectors does not exceed 2-3 wt.%.

The temperature regime also has a significant effect on the crystal growth rate (Fig.3). In this case, the estimation was based on the average crystal growth rate in the direction of pinacoid growth (0001).

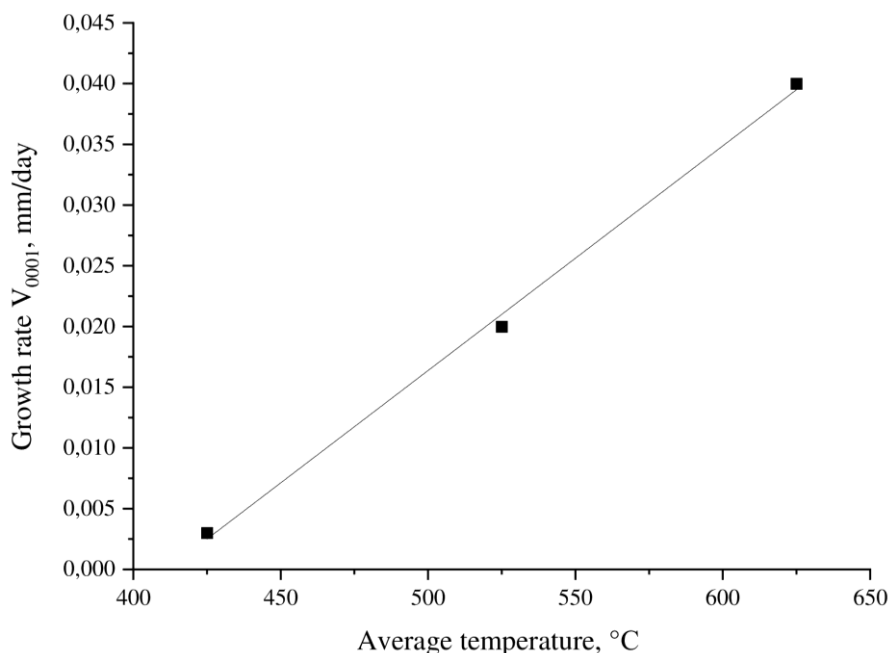


Fig.3 Dependence of the average growth rate V_{0001} on the average experiment temperature.

The crystal growth rate increases linearly with increasing temperature. The maximum value of the average growth rate is 0.04 mm/day at 600/650°C, which is ~20% less than the growth rate of crystals grown in fluoride solutions under similar PT-conditions.

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References

- Balitsky D.V., Balitsky V.S., Bondarenko G.V. Experimental study of crystallization conditions effect on germanium incorporation and distribution in synthetic quartz // *Vestnik Otdelenia nauk o Zemle RAN*. 2009. 1. 27.
- Balitsky V.S., Balitskaya L.V., Mar'ina E.A. Solubility and growth of quartz crystals in water-borate solutions // *Experiment in Geosciences*. 1998. 7. 1. p.56.
- Balitsky V.S., Balitsky D.V., Nekrasov, A.N., Balitskaya L.V., Bondarenko G.V., Samokhvalova O.L. Growth, structural-morphological features, and some properties of quartz-germanium oxide solid solution single crystals with quartz structure. // *Doklady Earth Sciences*. 2004. 396. 500-503.
- Balitsky, V.S., Balitsky, D.V., Pushcharovsky, D.Y. et al. Growth and morphology of high-germanium single crystals // *Doklady Earth Sciences*. 2017. 477. pp. 1437-1440.
- Godovikov A.A. *Mineralogia*. M.: Nedra., 1983. 647 p.
- Peretyazhko L.S., Smirnov S.Z., Kotel'nikov A.R., Kotel'nikova Z.A. Experimental study of the system H_3BO_3 -NaF-SiO₂-H₂O at 350-800°C and 1-2 kbar by the method of synthetic fluid inclusions // *Russian Geology and Geophysics*. 2010. 51. 4. pp. 450-472.
- Philippot E., Palmier D., Pintard M., Goiffon A. A General Survey of Quartz and Quartz-like Materials: Packing Distorsions, Temperature, and Pressure Effects // *Journal of Solid State Chemistry*. 1996. 123. pp. 1-13.
- Pichavant, M. Melt-fluid interaction deduced from studies of silicate-B₂O₃-H₂O system at 1 kbar // *Bulletin de Mineralogie*. 1983. 106, 201- 211.
- Ranieri V., Darracq S., Cambon M., Haines J., Cambon O., Largeteau A., Demazeau G. Hydrothermal Growth and Structural Studies of Si_{1-x}Ge_xO₂ Single Crystals // *Inorganic Chemistry*. 2011. 50. pp. 4632-4639.

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Synthetic phases of eudialyte composition.

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Abstract. Minerals, synthetic analogs of eudialyte, were synthesized hydrothermally at $T = 600^{\circ}\text{C}$ and $P = 2$ kbar from a stoichiometric mixture of Na_2CO_3 , CaO , Fe_2O_3 , ZrOCl_2 , and SiO_2 with $\text{Na}:\text{Ca}:\text{Fe}:\text{Zr}:\text{Si}$ corresponding to the end member of eudialyte $\text{Na}_{15}\text{Ca}_6\text{Fe}_3\text{Zr}_3\text{Si}(\text{Si}_{25}\text{O}_{73})(\text{OH})\text{Cl}_2 \cdot \text{H}_2\text{O}$, in the presence of 1M aqueous solutions of NaCl and NaF . Natural raslakite was added as a seed in an amount of 2 wt.% of the total mixture. The products were characterized by X-ray powder diffraction, IR and Raman spectroscopy, and electron probe microanalysis. Almost pure compounds of the eudialyte type were obtained in experiments with NaCl . Synthesis in the presence of a NaF solution led to the formation of an F-dominant eudialyte type compound, intergrown with raslakite as the main product and aegirine, vlasovite, and lalondeite as side products. All synthesized eudialytes are rich in Zr and deficient in Fe, as are the minerals of the eudialyte group from hyperagpaitic rocks related to foyaites.

Keywords: eudialyte, hydrothermal synthesis, crystal chemistry, peralkaline complexes

In the last years eudialyte-group minerals (EGM) have attracted increased attention of researchers due to an unusual combination of their qualities. Interest in these minerals is due to several reasons. On the one hand, they are relatively widespread. These are typical accessory (sometimes rock-forming) minerals of agpaitic complexes, numerous finds of them have already been made in dozens of alkaline massifs of the world. On the other hand, unlike most other rock-forming minerals, EGMs have the ability to concentrate a number of rare elements (Zr, Hf, Nb, REE). EGM are trigonal space groups $R\bar{3}m$, $R\bar{3}m$ or $R\bar{3}$, with unit cell parameters $a = 14.1 - 14.2$, $c = 30.0 - 30.8$ or ~ 60 Å.

General formula of EGM is: ($Z = 3$; Johnsen et al., 2003): $N1_3N2_3N3_3N4_3N5_3M1_6M2_{3-6}M3M4Z_3(\text{Si}_{24}\text{O}_{72})\text{O}'_{4-6}X1X2$, where $N1-5 = \text{Na}$, K , H_3O^+ , Ca , Mn^{2+} , Sr , Ba , *REE*; $M1 = \text{Ca}$, Mn^{2+} , Fe^{2+} , *REE*, Na , Sr ; $M2 = \text{Mn}^{2+}$, Fe^{2+} , Fe^{3+} , Na , Zr , Ta , Ti , K , H_3O^+ ; $M3$ и $M4 = \text{Si}$, S , Nb , Ti , W , Na ; $Z = \text{Zr}$, Ti , Nb ; $\text{O}' = \text{O}$, OH , H_2O ; $X1$ and $X2 = \text{F}$, Cl , H_2O , OH , CO_3 , SO_4 .

Eudialyte was first synthesized as a component of polymineral associations, including aegirine, vlasovite, and other zirconosilicates, from a mixture with the composition $6\text{SiO}_2 + \text{ZrO}_2 + 6\text{Na}_2\text{CO}_3 + \text{CaCO}_3 + \text{FeCl}_2 + 4\text{H}_2\text{O}$ in the presence of Na_2SiF_6 or K_2SiF_6 in the temperature range of $450-550^{\circ}\text{C}$ and H_2O at pressure from 85 to 700 bar (Christoph-Michel-Levy, 1961). In the cited paper, eudialyte was identified by powder X-ray diffraction (PXRD) data. It forms pseudo-hexagonal crystals about 50 μm across, which are almost optically isotropic, with a refractive index of 1.592.

Recently, the decomposition of eudialyte in various solvents was studied at 100°C for 48 h (Smirnova et al., 2015). In particular, it was shown that in hydrochloric acid from 2 to 10% complete

decomposition occurs. The interaction of eudialyte with 1-7% solutions of oxalic acid leads to leaching of Ca , Na and *REE*, while the zirconosilicate framework remains.

The experiments used a mixture of Na_2CO_3 , CaO , Fe_2O_3 , ZrOCl_2 and amorphous SiO_2 obtained by precipitation from a solution of tetraethyl orthosilicate (Trofimova et al., 2011). The $\text{Na}:\text{Ca}:\text{Fe}:\text{Zr}:\text{Si}$ ratio in the mixture corresponded to the final eudialyte element $\text{Na}_{15}\text{Ca}_6\text{Fe}_3\text{Zr}_3\text{Si}(\text{Si}_{25}\text{O}_{73})(\text{OH})\text{Cl}_2 \cdot \text{H}_2\text{O}$. Synthesis was carried out in high-pressure reactors with internal heating UVD-10000 designed by IEM RAS. The temperature and pressure control accuracy was $\pm 2^{\circ}\text{C}$ and ± 50 bar, respectively. The starting materials (150 mg of the sol-gel and 3 mg of the seed) were placed into platinum ampoules 50 mm long, 4–5 mm in diameter, and 0.1–0.2 mm thick in the wall. After that, the required amount of liquid was added, the ampoules were sealed, weighed, and checked for leaks.

In order to determine the role of chlorine in the formation of eudialyte, three synthesis experiments were carried out with different types and amounts of liquids: 100 ml of 1M NaCl (experiment 1), 150 ml of 1M NaCl (experiment 2), 100 ml of 1M NaF (experiment 3). The filled ampoules were placed in the reactors and kept at the required TP parameters (600°C and 2 kbar) for 10 days. The PT parameters were chosen based on data on the formation of eudialyte-bearing mineral complexes of the Lovozero alkaline massif (Kogarko et al., 2002). Quenching was carried out under isobaric conditions. After the experiments, the ampoules were weighed to control the tightness.

The products obtained during the experiments were fine-crystalline aggregates of a greenish-beige color. In the BSE images (Fig. 1-2), well-formed hexagonal crystals of newly formed eudialyte-type compounds are visible. Analytical data are given in table. 1. The product obtained in experiment 1 is close to the Khibiny type in terms of Ca content, but, in contrast to typical MGEs of type 1, is Fe-deficient and enriched in Zr. Taking into account the general crystal chemical regularities for EGM, we can conclude that the M2 region in the crystal structure of this compound has a mixed population ($\text{Fe} + \text{Zr} + \text{Na}$). For the EGM obtained according to experiment 2, two groups of local compositions can be distinguished, differing in the content of Ca and Fe . They correspond to the Ca-rich and Fe-deficient variety of eudialyte (experiment 2a) and the Fe-deficient Nb-free analogue of golyshevite (experiment 2b). Thus, these products are intermediate between the Fe-deficient analogues of type 1 and type 3.

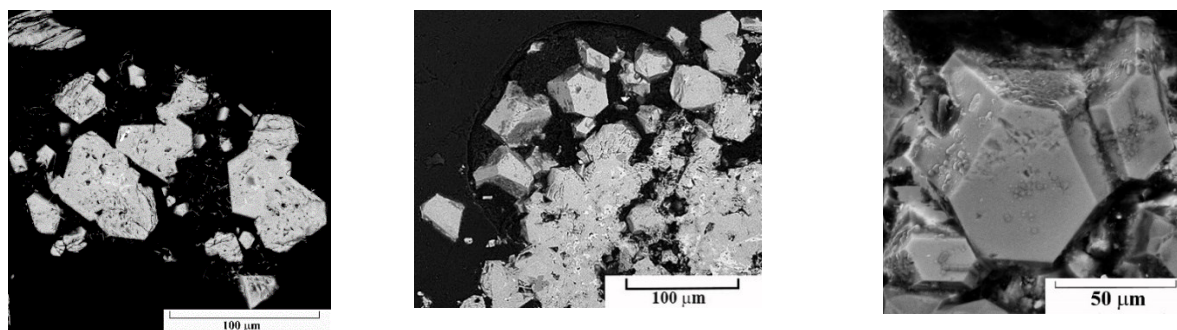


Fig. 1. Hexagonal crystals of synthesized compounds of the eudialyte type: (a) Experiment 1 (polished area), (b) Experiment 2a and (c) Experiment 2b.

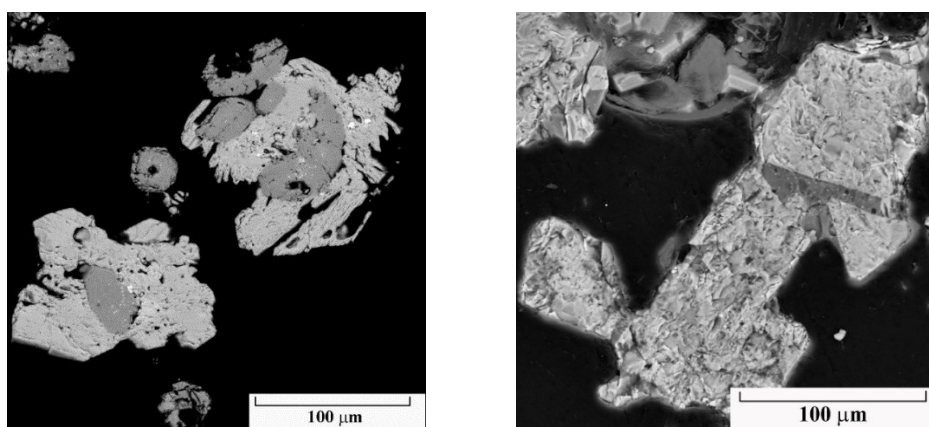


Fig. 2. Polished areas of the products obtained in run 3: (a) eudialyte type compound (light gray) and lalondeite (dark gray) and (b) crystals of eudialyte type compound (light gray) with aegirine inclusions (dark gray).

Table 1. Chemical composition (wt%) of synthesized eudialyte-type compounds (SD = standard deviation; bdl means “below detection limit”).

Component	Run 1		Run 2a		Run 2b		Run 3	
	Content	SD	Content	SD	Content	SD	Content	SD
Na ₂ O	14.76	0.54	12.95	1.04	13.37	0.30	15.59	0.65
CaO	10.77	2.01	13.20	0.57	16.17	0.46	9.10	0.64
FeO	2.88	0.40	3.74	0.33	2.48	0.78	2.26	0.48
SiO ₂	52.35	1.08	51.37	0.37	51.25	0.38	53.26	0.99
ZrO ₂	15.85	1.49	13.63	0.76	13.03	1.17	16.87	1.48
HfO ₂	0.06	0.13	0.35	0.36	0.10	0.19	0.17	0.25
Cl	0.99	0.25	1.03	0.20	1.15	0.16	0.27	0.20
F	bdl	-	bdl	-	bdl	-	0.79	0.29
-O=(Cl,F)	-0.22	0.06	-0.23	0.04	-0.26	0.04	-0.39	0.04
Total	97.43		96.02		97.29		97.93	
Formula coefficients calculated on 26 Si atoms								
Na	14.20		12.70		13.16		14.76	
Ca	5.72		7.16		8.78		4.76	
Fe	1.20		1.58		1.05		0.92	
Si	26.00		26.00		26.00		26.00	
Zr	3.84		3.37		3.22		4.02	
Hf	0.01		0.03		0.01		0.02	
Cl	0.83		0.88		0.99		0.23	
F	0		0		0		1.02	

