

Synthesis of minerals

Kotelnikov A.R., Suk N.I., Akhmedzhanova G.M., Drozhzhina N.A. Unit cell parameters of triple solid solutions of clinopyroxenes hedenbergite – diopside – aegirine. UDC 552.33:552.121+550.89:549.07

IEM RAS, Chernogolovka, Moscow district
(kotelnik@iem.ac.ru)

Abstract. Triple solid solutions of clinopyroxenes diopside – hedenbergite – aegirine were synthesized at $T=650-750^{\circ}\text{C}$ and $P=1.5-3.5$ kbar under fluid pressure (10% KF solution) on hydrothermal plants with external heating and a cold seal, as well as on gas condensers with a compressible medium (argon) with a duration of 14 to 45 days. The experimental products were studied by microprobe analysis and X-ray method. The dependences of the unit cell parameters of clinopyroxenes on their composition (mole fraction of magnesium) were obtained at a fixed content of the aegirine end member (~ 20 mol%). It is shown that solid solutions are not ideal. The parameters of the Margules model are calculated to describe the excess volumes of mixing of ternary solid solutions.

Keywords: *experiment, clinopyroxene, solid solutions, unit cell parameters*

Natural clinopyroxenes of various natural objects – igneous and metamorphic rocks – are often represented by solid solutions. In this work, an X-ray study of ternary solid solutions of clinopyroxenes: hedenbergite – diopside – aegirine was carried out. The purpose of this work is to study the dependence of the unit cell parameters (UCP) of clinopyroxenes on their composition (the mole fraction of magnesium) at a fixed content of the aegirine end member (~ 20 mol%).

Experimental method. For the synthesis of ternary solutions, gel mixtures of end minerals were used. Clinopyroxenes of the Hed-Di-Aeg system are characterized by the presence of both ferrous and ferric iron. Since the synthesis of gel mixtures with a given $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was impossible, we worked with mixtures of separately prepared Hed, Di, and Aeg gels. Previously, hedenbergite gel was reduced in a hydrogen flow at 550°C for 2 hours. The experiments were carried out in gold ampoules, 10% KF solution was used as a fluid. The ratio of sample:fluid in the experiments was 8-15. Synthesis experiments were carried out at $650-750^{\circ}\text{C}$, pressure 1.5-3.5 kbar. The experiments were carried out on hydrothermal installations with external heating and a cold seal, as well as on gas condensers with a compressible medium – argon. All equipment designed by IEM RAS. Temperature and pressure control were carried out with errors in temperature

$\pm 2^{\circ}\text{C}$, pressure ± 0.05 kbar. The duration of the experiments ranged from 14 to 45 days. The experimental products were studied by microprobe analysis.

Experimental results. It was shown that the ternary solid solutions of clinopyroxenes are characterized by the content of the aegirine end member, on average, 20.0 ± 2.2 mol.%. The compositions of synthetic clinopyroxenes correspond to the stoichiometric formulas of the ternary system (Di-Hed-Aeg). An x-ray study of the samples was carried out to refine the UCP. Silicon was used as an internal standard. The polygonal reflection correction method was used. The unit cell parameters of triple clinopyroxenes of the Di – Hed – Aeg system (content of the aegirine end member $X_{\text{Aeg}}^{\text{Cpx3}} \sim 0.2$) are given in Table 1.

The concentration dependences of UCP on the composition of clinopyroxenes were obtained. They are described by equations of the form: $a = a_0 + a_1 \cdot x + a_2 \cdot x^2 + a_3 \cdot x^3$. The values of parameters $a_0 - a_3$ are given in Table 2.

The concentration dependences of parameter “a” and cell volume “V” are shown in Figs. 1a, b. It can be seen that the unit cell volume has a sign-alternating deviation from the ideal one. Thus, it has been shown that the solid solutions of triple clinopyroxenes are not ideal. Calculated parameters of the Margules model for describing excess mixing volumes of ternary solutions: $V^{\text{e}} = x^2 \cdot (1-x) \cdot W_1 + (1-x)^2 \cdot x \cdot W_2$. $W_1 = 14.98 \pm 2.3$ [A]; $W_2 = -18.14 \pm 1.1$ [A].

Conclusions

1. Triple solid solutions of clinopyroxenes have been synthesized in the system diopside – hedenbergite – aegirine, at a mole fraction of the aegirine end member of 20 mol.%.

2. The unit cell parameters of the synthesized clinopyroxenes have been refined. It is shown that the concentration dependences of the unit cell parameters on the mole fraction of magnesium are quite well described by polynomials of the 3-rd degree.

3. It is shown that solid solutions of the Di-Hed-Aeg system are not ideal; to describe the excess volumes of mixing, the parameters of the Margules model are calculated.

The work was supported by the FMUF-2022-0002 program.

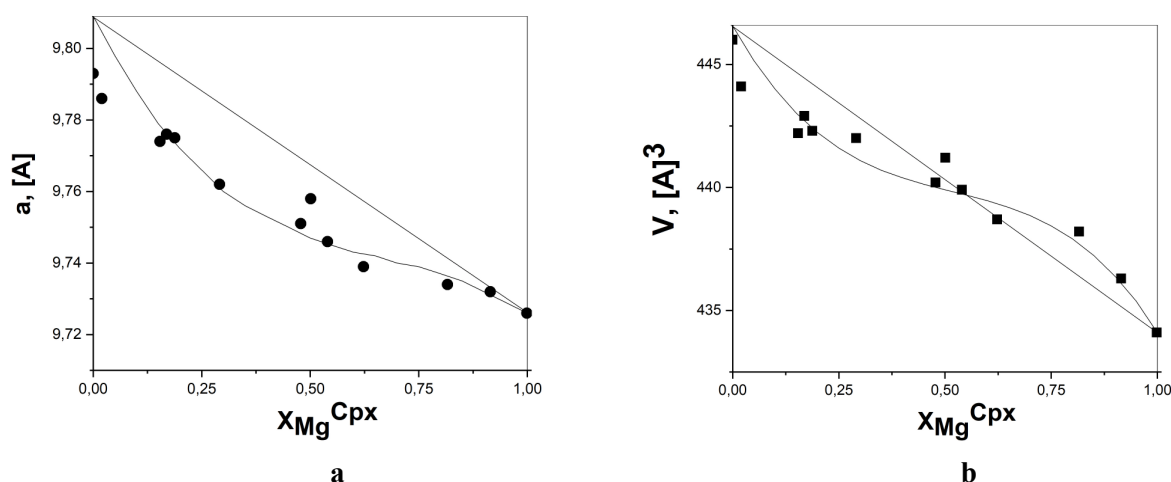
Table 1. Unit cell parameters of ternary solid solutions of clinopyroxenes in the diopside-hedenbergite-aegirine system.

Aeg, mol.%	Hed, mol.%	Di, mol.%	X _{Mg} ^{Cpx}	a, [Å]	b, [Å]	c, [Å]	β, [°]	V, [Å] ³	n ¹⁾
20	80	0	0.0	9.793	8.966	5.270	105.50	446.0	-
20	80	0	0.0	9.821	8.984	5.253	105.17	447.3	33
19.8	78.6	1.6	0.02	9.786	8.961	5.255	105.47	444.1	44
28.6	60.4	11	0.154	9.774	8.940	5.256	105.69	442.2	37
16.5	69.3	14.1	0.169	9.776	8.957	5.252	105.62	442.9	49
18.2	66.4	15.4	0.188	9.775	8.948	5.252	105.68	442.3	46
12.5	62.0	25.5	0.291	9.762	8.934	5.265	105.72	442.0	42
21.2	41.1	37.7	0.478	9.751	8.916	5.265	105.90	440.2	36
20.5	39.7	39.8	0.501	9.758	8.906	5.269	105.94	441.2	22
24.3	34.8	40.9	0.540	9.746	8.930	5.251	105.77	439.9	41
21.9	29.4	48.7	0.623	9.739	8.912	5.254	105.85	438.7	50
20.8	14.5	64.7	0.816	9.734	8.909	5.254	105.89	438.2	48
16.0	7.1	76.9	0.915	9.732	8.916	5.227	105.83	436.3	38
20.1	0.1	79.8	0.999	9.726	8.919	5.215	106.34	434.1	31

Note. 1) the number of reflections used to refine the unit cell parameters.

Table 2. Polynomial coefficients for describing the concentration dependences of the unit cell parameters of ternary solid solutions of clinopyroxenes.

Parameter	a0	a1	a2	a3	S _x	E _x	R ²
a, [Å]	9.80949	-0.24233	0.31650	-0.15813	0.008	0.004	0.941
b, [Å]	8.97691	-0.18396	0.12836	-0.00216	0.006	0.003	0.956
c, [Å]	5.25671	-0.03227	0.16894	-0.17874	0.005	0.003	0.909
β, [°]	105.268	3.56906	-7.36046	4.81389	0.106	0.052	0.917
V, [Å] ³	446.559	-30.4237	50.4429	-32.4174	0.640	0.341	0.979


Fig. 1. Dependences of the unit cell parameters of clinopyroxenes on their composition: (a) parameter “a” and (b) cell volume “V”. Dots show experimental data

Kotelnikov A.R.¹, Shchekina T.I.², Suk N.I.¹,
 Kotelnikova Z.A.³, Antonovskaya T.V.⁴
**Structural ordering of feldspars as an
 indikator of the temperature of
 mineralogenesis** UDC 552.08:550.89

¹IEM RAS, Chernogolovka, Moscow district; ²MSU, Geol. faculty, Moscow; ³IGEM RAS, Moscow; ⁴City of Ukhta (kotelnik@iem.ac.ru)

Abstract. An experimental study of the ordering of albite at a temperature of 200 to 400°C and a pressure of 200 to 1000 bar for up to 60 days in autoclaves with a heat-sealed shutter has been carried out. Glasses and gels of albite composition were used as starting materials. The experiments were carried out according to the ampoule method in slightly alkaline solutions with the addition of a certain amount of amorphous silica to the sample. After the experiments, an X-ray study of feldspars was carried out, the unit cell parameters and ordering parameters were refined. The dependence of parameter Δ131 on temperature is shown. For a number of natural

parageneses containing feldspars, the temperature was estimated from the structural state of feldspars.

Keywords: *experiment, albite, feldspars, unit cell parameters*

The processes of ordering in feldspars – the redistribution of aluminum between nonequivalent positions of the crystal structure – can serve as an indicator of the temperature of formation. For the first time, quantitative data on the relationship between structural parameters and the degree of ordering for plagioclases were obtained in (Bambauer et al., 1967). Subsequently, a number of experimental studies were carried out on the ordering of feldspars in the temperature range from 350 to 1000°C. The research data are presented in Table 1 and in Fig. 1a. However, in the region of low temperatures (less than 400 °C), there is not enough data. Therefore, the purpose of our work was to experimentally study the ordering of albite at a temperature of 400 - 150 °C (P=0.2 ÷ 1 kbar).

Our experiments were carried out under hydrothermal conditions using the ampoule technique. Glasses and gels of albite composition were used as starting materials. The ordering of albites was carried out in weakly alkaline solutions with the addition of a certain amount of amorphous

silica to the sample. We used autoclaves designed by IEM RAS and hydrothermal high pressure plants with external heating and a cold seal. The temperature control accuracy was ±3 °C, the pressure was set by the filling factor of the autoclaves with an accuracy of 0.1 kbar. The duration of the experiments was up to 60 days, depending on the TP-parameters. The composition of feldspars was determined by the microprobe method. We also carried out an X-ray study of feldspars, refinement of the unit cell parameters and ordering parameters. The dependence of the parameter Δ131(Cu-K_α) on temperature is shown. The results of X-ray studies of albites are shown in Figs. 1b and in Table 2.

Based on our experimental data and results of works (McKenzie, 1957; Eberhard, 1967; Martin, 1969; Senderov et al., 1971; Senderov and Shchekina, 1976; Mason, 1979; Kroll and Muller, 1980; Kotelnikov, 1995; 2011) an equation was derived to calculate the temperature using the parameter Δ131 (Cu-K_α) for albites:

$$T^{\circ}\text{C} / 1000 = -11.794 + 24.0798 * (d131) - 15.7357 * (d131)^2 + 3.44235 * (d131)^3 (\pm 20^{\circ}\text{C}) \quad (1),$$

where d131 – parameter Δ131 (Cu-K_α).

Table 1. Experimental data on the structural ordering of albites at various temperatures

T, °C	Δ131 (Cu-K _α)	reference	T, °C	Δ131 (Cu-K _α)	reference
1000	2.01	1	550	1.76	6
900	1.98	2	550	1.59	7
850	1.95	2	500	1.43	3
800	1.92	2	500	1.42	2
800	1.94	3	500	1.40	5
800	1.88	4	500	1.60	6
750	1.89	3	500	1.32	7
700	1.83	3	500	1.24	4
700	1.87	4	475	1.26	7
625	1.78	5	450	1.49	6
600	1.78	5	450	1.20	7
600	1.78	6	400	1.28	6
600	1.80	4	400	1.20	7
550	1.60	3	350	1.25	6
550	1.50	5	350	1.17	7

Note:

1) Kroll&Muller, 1980; 2) McKenzie, 1957; 3) Eberhard, 1967; 4) Kotelnikov, 1995; 5) Mason, 1979; 6) Martin, 1969; 7) Senderov et al., 1971.

Table 2. Unit cell parameters of albites synthesized under hydrothermal conditions (T= 150 ÷ 450°C; P = 0.5–1.0 kbar) in the presence of sodium hydroxide and sodium silicate solutions.

T, °C	P ¹⁾	a, [Å] ²⁾	b, [Å]	c, [Å]	α, [°]	β, [°]	γ, [°]	V, [Å] ³	Δ131 ³⁾
150	0.2	8.135	12.781	7.161	94.30	116.61	87.57	663.7	1.070
200	0.5	8.136	12.786	7.159	94.26	116.59	87.69	664.1	1.101
200	0.5	8.137	12.788	7.159	94.25	116.60	87.71	664.2	1.087
200	0.5	8.137	12.787	7.159	94.26	116.60	87.69	664.2	1.102
250	0.5	8.137	12.787	7.159	94.27	116.60	87.70	664.2	1.107
250	0.5	8.139	12.786	7.159	94.26	116.61	87.70	664.2	1.092
250	0.5	8.136	12.783	7.160	94.29	116.59	87.65	664.0	1.091
400	1	8.141	12.795	7.154	94.21	116.60	87.96	664.6	1.211

T, °C	P ¹⁾	a, [Å] ²⁾	b, [Å]	c, [Å]	α, [°]	β, [°]	γ, [°]	V, [Å] ³	Δ131 ³⁾
400	1	8.140	12.793	7.154	94.20	116.60	87.97	664.4	1.210
425	1	8.140	12.795	7.152	94.16	116.58	88.08	664.4	1.242
425	1	8.140	12.791	7.151	94.12	116.57	88.11	664.3	1.244
450	1	8.141	12.802	7.148	94.11	116.57	88.20	664.5	1.278
450	1	8.141	12.802	7.146	94.09	116.55	88.23	664.5	1.283

Note: 1) pressure (kbar); 2) values of elementary cell parameters are given in angstroms, angles – in degrees; 3) Δ131 – interangular distance between reflections 131 and 1-31 for (Cu-K_α).

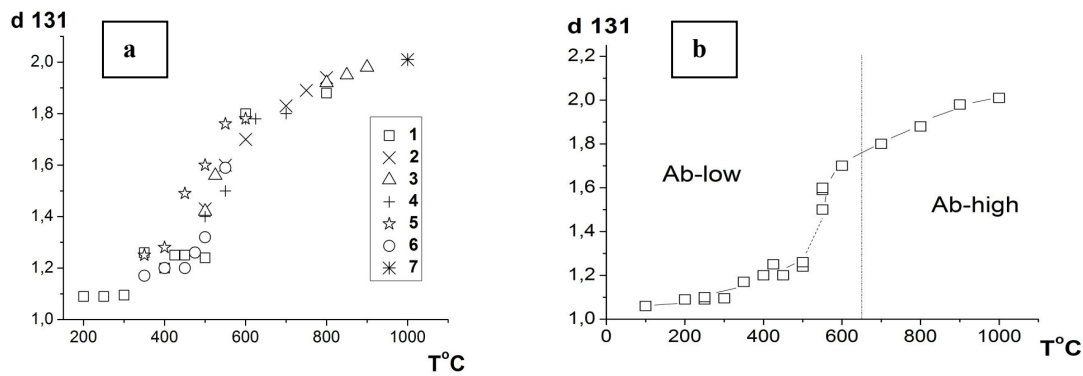


Fig.1. Ordering of albite depending on temperature, according to various works (a); structural transition high-low albite according to the work (Senderov, Shchekina, 1976) (b).

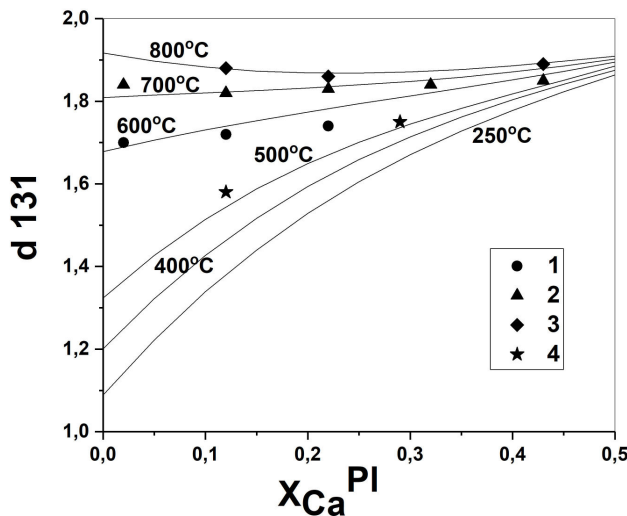


Fig. 2. Dependence of plagioclase compositions on the parameter Δ131 (Cu-K_α). (Eberhard E., 1967): 1 – 600°C, 2 – 700°C, 3 – 800°C; (Kotelnikov, 1995): 4 – 500°C.

When deriving and refining the parameters of the above equation, we used data passing according to statistical criteria (deviation of outliers).

Fig. 2 shows a diagram of the composition of plagioclases – the parameter Δ131 (Cu-K_α) for estimating the temperature from the degree of ordering of feldspars. To estimate the temperature by the value of Δ131 (Cu-K_α), equations of the form were used:

1) in the range of compositions An₅-An₃₅:
 $T^{\circ}C/1000 = a_0 + a_1*d131 + a_2*(d131)^2 + a_3*(d131)^3 + 0.007$; where d131 – parameter Δ131 (Cu-K_α); in turn, the parameters a₀ ... a₃ are calculated according to the following equations depending on the plagioclase composition:

$$a_0 = -8.859 + 9.225*X - 2553,6*X^2 + 3076.5*X^3;$$

$$a_1 = 18.026 - 12.504*X + 4590.625*X^2 - 6570.04*X^3;$$

$$a_2 = -11.658 + 2.93708*X - 2721.97*X^2 + 4401.79*X^3;$$

$$a_3 = 2.545 + 0.72129*X + 532.577*X^2 - 944.20*X^3;$$

where X – mole fraction of calcium in plagioclase.

2) in the range of compositions An₃₆-An₅₀ :
 $T^{\circ}C/1000 = b_0 + b_1*d131 + b_2*(d131)^2 - 0.044$; where d131 – parameter Δ131 (Cu-K_α); in turn, the parameters b₀ ... b₂ are calculated according to the following equations depending on the plagioclase composition:

$$b_0 = 4441.35 - 35604*X + 95925.8*X^2 - 87400*X^3;$$

$$b_1 = -4488 + 36002.84*X - 97121.8*X^2 + 88628*X^3;$$

$b_2 = 1132.17 - 9087.24 \cdot X + 24547.7 \cdot X^2 - 22439.5 \cdot X^3$; where X – mole fraction of calcium in plagioclase.

A computer program has been developed to calculate the temperature with an error of $\pm 25^\circ\text{C}$. This program can be used in the range of plagioclase compositions ($X_{\text{Ca}}^{\text{Pl}}$) from 0.05 to 0.5 ($\text{An}_5 - \text{An}_{50}$). At lower values of the calcium content of plagioclases, equation (1) works better.

For a number of natural parageneses containing feldspars (Rogozhnikovskoe uplift, Western Siberia, Salma pluton (rapakivi granites) and metamorphic rocks of Finalva, Senja Island, Polar Norway), the temperature was estimated from the structural state of feldspars and other thermometers. The data are shown in Table 3. Good convergence of the results of mineral thermometry performed for various types of rocks is shown.

Table 3. Temperature estimates using the parameter $\Delta 131$ (Cu-K_a) and comparison with other mineral thermometers.

Formation	Paragenesis	Thermometers	Interval T°C	$\Delta 131$
Paleovolcanites, Rogozhnikovskoe uplift, Western Siberia	Ab+Chl+Qz+Cb	Chl, Pl-Ksp ¹⁾	220 ÷ 630 ²⁾	Ab: 1.24 ³⁾ (430°C)
Salma pluton, rapakivi granites, Pitkyaranta, Karelia	Ab+Ksp+Pl+Qz	Pl-Ksp	400±40	Ab: 1.183 370°C) Pl(An_{16}): 1.486 (325°C)
Finalva, metamorphites, Senja Island, Polar Norway	Bi+Gr+Ksp+Pl +Chl+Qz	Chl, Pl-Ksp	420 ÷ 250	Pl: 1.537 (323°C)

Note. Ab – albite; Cb – carbonate; Chl – chlorite; Ksp – potassium feldspar; Pl – plagioclase; Qz – quartz. 1) Thermometers: Chl – chlorite; Pl-Ksp – two-feldspar; 2) temperature determined by geothermometers; 3) parameter $\Delta 131$ (Cu-K_a); the temperature estimated from the degree of feldspar ordering is given in parentheses.

The work was supported by the FMUF-2022-0002 program.

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Kotelnikov A.R., Suk N.I., Akhmedzhanova G.M. Study of solid solutions of Ga-containing feldspars UDC 550.4:549.651.1

IEM RAS, Chernogolovka, Moscow district
(kotelnik@iem.ac.ru)

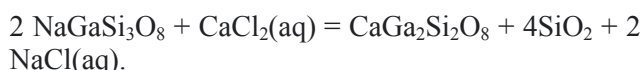
Abstract. Ga-bearing feldspars were synthesized under hydrothermal conditions at T=550°C and P=1.5 kbar. X-ray studies have shown the structural ordering of the obtained feldspars. Cation-exchange experiments were also carried out in the gallium albite – fluid system at T=550°C and P=1.5 kbar. Studied reaction: $2 \text{NaGaSi}_3\text{O}_8 + \text{CaCl}_2(\text{aq}) = \text{CaGa}_2\text{Si}_2\text{O}_8 + 4\text{SiO}_2 + 2 \text{NaCl}(\text{aq})$.

The experimental products were analyzed by microprobe and X-ray analysis. The composition of the solution was determined by atomic absorption analysis. It is shown that the following phases are present in cation exchange experiments: (1) (Na,Ca)-gallium feldspar; (2) gallium paracelsian (composition CaGa₂Si₂O₈); (3) quartz. The unit cell parameters of the synthesized phases are determined.

Keywords: synthesis, Ga-containing feldspars, unit cell parameters

The synthesis of gallium-containing feldspars was carried out under hydrothermal conditions at a temperature of 550 °C and a pressure of 1.5 kbar. Glasses of NaGaSi₃O₈ and KGaSi₃O₈ compositions obtained by melting oxide mixtures at a temperature of 1200 - 1300 °C were used as starting materials. Gallium analogs of albite and microcline were obtained by glass recrystallization. X-ray studies have shown the structural ordering of the obtained feldspars.

Cation exchange experiments were also carried out in the system gallium albite – fluid at T=550°C and P=1.5 kbar. The reaction has been studied:



The compositions of the initial solutions were set as mixtures of 1 M NaCl and CaCl₂ solutions. The

experiments were carried out in gold ampoules of 7 mm in diameter in hydrothermal installations with external heating and a cold seal. The accuracy of temperature regulation and control was ± 2 °C, pressure ± 0.05 kbar. The duration of the experiments ranged from 21 to 30 days. The experimental products were analyzed by microprobe and X-ray analysis. The composition of the solution was determined by atomic absorption analysis on a Kvant-4M instrument. The conditions and results of the experiments are given in Table 1.

It is shown that the following phases are present in experiments on cation exchange: (1) (Na,Ca) - gallium feldspar; (2) gallium paracelsian (composition $\text{CaGa}_2\text{Si}_2\text{O}_8$); (3) quartz (Fig. 1). The unit cell parameters of gallium feldspars and paracelsian are presented in Table 2.

It is possible to estimate the dependence of the unit cell parameters of gallium plagioclases on the

composition. According to the data given in Table 2, the following second-order equations were calculated as the form: $P = A_0 + A_1 \cdot X + A_2 \cdot X^2$; where P is the unit cell parameter, X is the mole fraction of calcium in the solid solution. The values of the polynomial coefficients are given in Table 3.

According to the work of N.S. Vasiliev (1990), synthetic gallium albites are almost completely structurally ordered varieties. Since gallium plagioclases are structural analogs of aluminosilicon ones, one can use the interangular distance $\Delta 131(\text{Cu-K}\alpha)$ proposed in (Bambauer et al., 1967) to assess their structural state. The values of $\Delta 131$ are given in Table 2, the dependence of this parameter on the composition is shown: $\Delta 131(\text{Cu-K}\alpha) = 0.986 + 0.2154 \cdot X + 5.0294 \cdot X^2$; $S_x = 0.02$ (X is the mole fraction of calcium in the solid solution).

Table 1. Conditions and results of experiments on cation exchange gallium feldspar – fluid (T=550 °C and P=1.5 kbar).

№ exp.	Initial weight	Initial solution	Phase composition of products	$X_{\text{Ca}}^{\text{Pl}}$	$X_{\text{Ca}}^{\text{II}}$	K_D
7473	100 mg glass Ga-Ab	400 mkl 1M NaCl	Ga- Ab ¹⁾	0	0	-
7465	75 mg glass Ga-Ab	150 mkl 1M NaCl+ 50 mkl 1M CaCl ₂	Ga-Pl + Pcn + Qz	0.12	0.062	2.199
7464	90 mg glass Ga-Ab	70 mkl 1M NaCl+ 150 mkl 1M CaCl ₂	Ga-Pl + Pcn + Qz	0.15	0.075	2.368
7467	100 mg glass Ga-Ab	150 mkl 1M NaCl+ 150 mkl 1M CaCl ₂	Ga-Pl + Pcn + Qz	0.20	0.275	0.597
7462	100 mg glass Ga-Ab	300 mkl 1M CaCl ₂	Pcn + Qz	-	-	-

Note. 1) mineral indices: Ga-Ab – gallium albite; Ga-Pl – gallium plagioclase; Pcn – paracelsian; Qz – quartz.

Table 2. Unit cell parameters of Ga-feldspars of the $\text{NaGaSi}_3\text{O}_8 - \text{CaGa}_2\text{Si}_2\text{O}_8$ series and gallium para-celsian (exp. 7462).

№ exp.	$X_{\text{Ca}}^{\text{Fsp}}$	a, [Å]	b, [Å]	c, [Å]	α , [°]	β , [°]	γ , [°]	V, [Å] ³	$\Delta 131$ (Cu-K α)
7196	0.00	8.170	12.860	7.198	94.32	116.49	87.28	674.9	0.915
7473	0.00	8.152	12.850	7.180	94.35	116.46	87.39	671.3	0.988
7465	0.12	8.167	12.856	7.183	94.13	116.36	87.78	674.0	1.066
7464	0.15	8.170	12.860	7.187	94.16	116.32	87.93	675.1	1.156
7467	0.20	8.171	12.882	7.182	94.01	116.38	88.22	675.6	1.224
7462	-	8.736	9.386	8.305	90.0	89.50	90.0	681.0	

Table 3. Values of the polynomial coefficients for describing the concentration dependences of the unit cell parameters of gallium plagioclases.

Cell parameters	A0	A1	A2	R ²	S_x
a, [Å]	8.152	0.1783	-0.41176	0.998	0.001
b, [Å]	12.850	-0.1477	1.5196	0.986	0.002
c, [Å]	7.180	0.0838	-0.348	0.619	0.003
α , [°]	94.35	-1.347	-1.3725	0.940	0.03
β , [°]	116.46	-1.8321	6.9608	0.912	0.02
γ , [°]	87.39	1.9166	11.1765	0.999	0.01
V, [Å] ³	671.3	28.263	-31.372	0.988	0.21

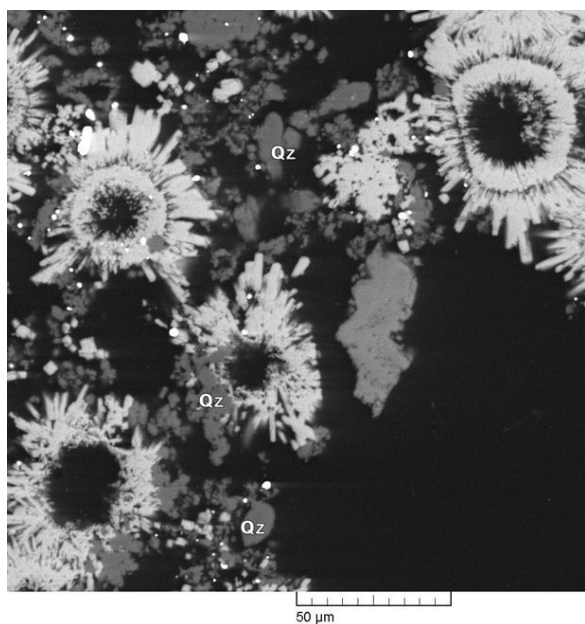


Fig. 1. Products of experiment 7462. Light coronary crystals – paracelsian ($\text{CaGa}_2\text{Si}_2\text{O}_8$). Qz - quartz.

The distribution of sodium and calcium in the system of gallium plagioclase – water-salt solution at 550°C and $P=1.5$ kbar is imperfect. The distribution coefficient of Ca changes from ~ 2.3 to 0.6 with an increase in the mole fraction of calcium in the fluid. The dependence of $\ln(KD)$ on the composition of the solid solution is shown: $\ln(KD) = 3.111 - 14.446 \cdot X$; $S_x=0.3$; where X is the mole fraction of calcium in the solid solution.

This fact testifies to the deviation of the $\text{NaGaSi}_3\text{O}_8 - \text{CaGa}_2\text{Si}_2\text{O}_8$ solid solution from the ideal one. This conclusion is determined by the ideal behavior of an aqueous solution of 1M NaCl - CaCl_2 at given TP-parameters – according to the results of experimental work (Orville, 1972; Delbov, 1978; Kotelnikov et al., 1981, Dujon & Lagache, 1984; Kotelnikov, Shchekina, 1986, Shvedenkova, Shvedenkov, 1990).

Conclusions

1. The existence of $\text{NaGaSi}_3\text{O}_8 - \text{CaGa}_2\text{Si}_2\text{O}_8$ solid solution in the range of compositions $X_{\text{Ca}}^{\text{pl}} = 0.0 - 0.20$ is shown.

2. In almost all experiments containing calcium, the presence of a paracelsian phase is noted, which forms coronal rims after gallium plagioclases.

3. The parameters of the unit cells of the solid solutions of gallium plagioclases are refined, their dependence on the composition is shown.

4. The dependence of the distribution coefficient of calcium between gallium plagioclases and water-salt fluid is determined, and the nonideality of the solid solution is shown.

The work was supported by the FMUF-2022-0002 program.

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Setkova T.V., Spivak A.V., Balitsky V.S., Bublikova T.M. Synthesis and spectroscopic studies of $\text{NaGaSi}_3\text{O}_8$ crystals with albite structure UDC: 54.057:543.42

D.S. Korzhinskii Institute of Experimental Mineralogy RAS, Chernogolovka e-mail: setkova@iem.ac.ru

Abstract. Crystals of $\text{NaGaSi}_3\text{O}_8$ of 200 μm in size with an albite structure were obtained at hydrothermal conditions at temperature of 650°C and pressure of 100 MPa. The crystals have a lamellar habit, and form single crystals or polycrystalline intergrowths. Raman spectra of natural and synthetic albite were compared with gallium analogues. The shift of the main bands in the Raman spectra was established depending on the composition.

Keywords: albite, gallium, hydrothermal synthesis, Raman spectroscopy.

Feldspars, including albite and the gallium analogue of albite, as representatives of framework aluminosilicates, are potential matrix minerals for the immobilization of radionuclide elements and other industrial wastes (Kotelnikov et al. 1995). The synthesis of gallium albite has been described in detail (Smith, 1974; Kotelnikov et al. 2021), however

its spectroscopic characteristics in comparison with natural samples remain unstudied. The aim of this work was to carry out the synthesis of single crystals of albite and its gallium analogue, and to compare their Raman spectroscopic characteristics with natural albites of various compositions.

The crystals were synthesized in 2 ml gold ampoules under hydrothermal conditions at a temperature of 650°C and a pressure of 100 MPa using a special methodological approach consisting of in using quartz rods as the crystallization surface. Another charge component was added in the powered state in the form of an oxide (Al_2O_3 or Ga_2O_3). The ampoule was filled with a solution of 5 wt. % NaOH in an amount corresponding to the filling factor. The duration of the experiments was 14 days. For further comparison, samples of natural albite were taken from the Altai (sample **Z-12-69**) and from the watershed vein of the Malkhan field, Transbaikalia (sample T-7-06).

The composition of the synthesized and natural

albite crystals was studied using a CamScanM2300 scanning electron microscope (VEGA TS 5130MM) with a Link INCA Energy-350 spectral analyses (Table 1). Raman spectroscopy was used to study the structural features of natural and synthetic varieties of albite at ambient conditions. Raman spectra of albites were measured using the apparatus consisting of spectrograph Acton SpectraPro-2500i with a detector cooling up to -70°C CCD Pixis2K and the microscope Olympus with a continuous solid-state monomeric laser with radiation wavelength 532 nm and diode pumping at IEM RAS. The laser beam diameter was 3–5 μm . Spectral range of split was 3.8 cm^{-1} . Raman data were collected by repeated exposures of 540 s (3×180 s). The software Fytk 1.3.1 was used for profile fitting for the Raman band analysis.

Colorless lamellar crystals of albite up to 500 μm in size and Ga-albite up to 200 μm in size were obtained (Fig. 1). The crystals were formed as intergrowths mainly on the surface of the quartz rod.

Table 1. Chemical composition of natural and synthetic albites

Sample	Z-12-69	T-7-06	Ab (syn)	Ga-Ab (syn)
Component	wt%			
Na_2O	10.82	10.10	10.91	11.33
SiO_2	69.95	66.56	68.41	59.88
Al_2O_3	20.15	19.77	19.11	0.00
Ga_2O_3	0.00	0.00	0.00	28.25
CaO	0.15	0.72	0.00	0.00
Total	101.07	97.14	98.43	99.65

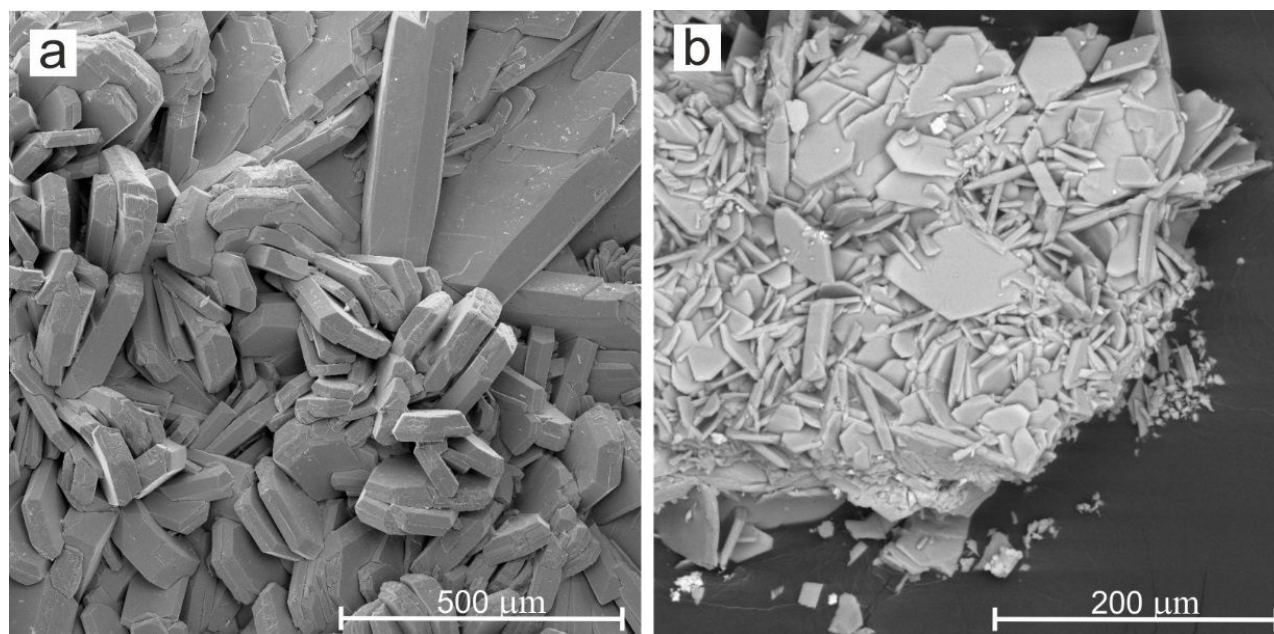


Fig. 1. Cluster crystals of synthetic albite **Ab (syn)** (a) and Ga-albite **Ga-Ab (syn)** (b).

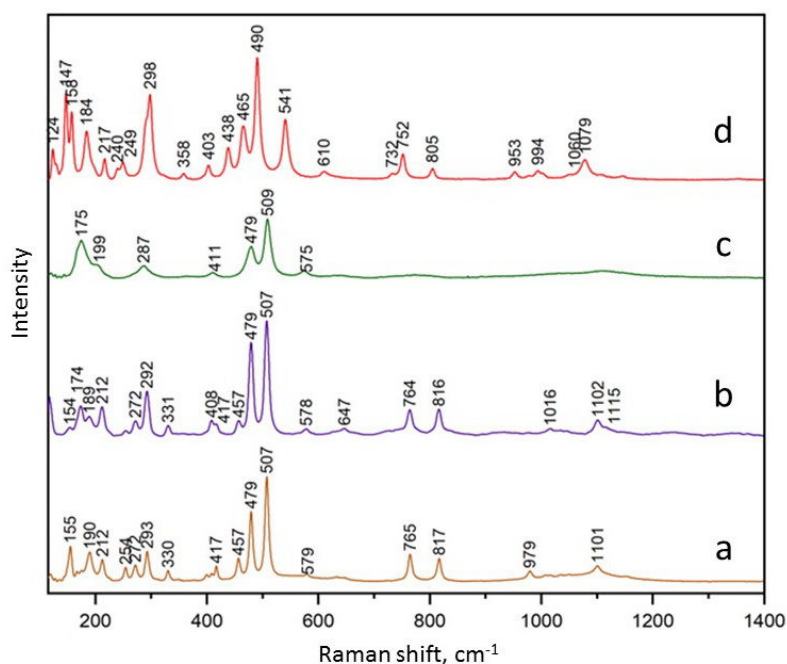


Fig. 2. Raman spectra of natural **Z-12-69** (a), **T-7-06** (b) and synthetic **Ab (syn)** (c), **Ga-Ab (syn)** (d) albites at ambient conditions.

The Raman spectra of natural and synthetic albites were obtained in the range of 100-1400 cm⁻¹, in which there are bands of different intensities (Fig. 2). The spectra of natural and synthetic albites show a similar topology. In this case, there is a general shift towards the region of lower frequencies of all fundamental modes of the Raman spectrum of synthetic Ga-albite compared to natural and synthetic NaAlSi₃O₈ albites. In the low frequency range up to ~300 cm⁻¹ (Na environment breathing rotation and rotational and translational vibrations of 4 tetragonal rings) this shift is ~5 cm⁻¹, in the range of 330-600 cm⁻¹ (breathing-deformation vibrations of 4 tetragonal rings) – 15-20 cm⁻¹ with the appearance of a new peak at 541 cm⁻¹, which may be due to the substitution of aluminum by gallium in the crystal structure. In the region of tetrahedral deformation 600-900 cm⁻¹ the shift is ~10 cm⁻¹, in the region of tetrahedral breathing vibrations O-T-O, T-O (T=Si, Al/Ga) 900-1200 cm⁻¹ the shift is ~ 20 cm⁻¹.

As a result of work, under hydrothermal conditions at a temperature of 650 °C and a pressure of 100 MPa, crystals of pure NaAlSi₃O₈ and gallium NaGaSi₃O₈ albite were obtained. The crystals have a lamellar habit and are formed on the surface of a quartz rod in the form of individual crystals and clusters. Comparison of the Raman spectra of natural and synthetic albites showed a shift in the main bands depending on the composition.

This study is fulfilled under Research program № FMUF-2022-0002 of the Korzhinskii Institute of Experimental Mineralogy.

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Spivak A.V.^{1,*}, Setkova T.V.¹, Gorelova L.A.², Vereshchagin O.S.², Kovalev V.N.^{1,2}, Zakharchenko E.S.¹, Borovikova E.Yu.³
Synthesis and high-temperature behavior of Ga₃GaGeO₈ UDC 54.057:543.42

¹D.S. Korzhinskii Institute of Experimental Mineralogy of Russian Academy of Sciences, Chernogolovka, Russia; ²Institute of Earth Sciences, Saint Petersburg State University, St. Petersburg, Russia; ³Lomonosov Moscow State University, Moscow, Russia; spivak@iem.ac.ru

Annotation. β-Ga₃GaGeO₈ crystals up to 100 μm in size were obtained under thermogradient hydrothermal conditions at a temperature of 600/650°C and a pressure of 100 MPa. Crystals have a dipyrmidal habit and form twins. It was shown by the Rietveld method that the synthesized compound belongs to the structural type Fe₃Ge₂O₈ (sp. gr. *P2₁/c*) with lattice parameters *a* =

8.2714(2), $b = 8.2402(2)$, $c = 9.0900(2)$ Å, $\beta = 117.676(1)^\circ$, $V = 548.67(2)$ Å³ ($R_{wp} = 2\%$). The crystal structure is based on layers of edge-connected GaO₆ octahedra, which, when connected through GeO₄ and GaO₄ tetrahedra form a framework. The effect of temperature (25–600 °C) on the crystal structure of the synthesized compound was studied by *in situ* Raman spectroscopy. The shift of the main bands of the spectrum to the region of low frequencies was shown. No polymorphic transitions were found in the studied temperature range.

Keywords: gallium, germanium, germanates, hydrothermal synthesis, Raman spectroscopy.

Gallium germanates can be considered as structural analogues of silicates and aluminosilicates, which are of great importance in the Earth sciences. At the same time, some of the Ga,Ge-containing compounds obtained so far have no analogues in nature. Due to their unique physical and chemical properties, such compounds are also of interest for materials science. For example, Ga₄GeO₈ powders doped with Tb³⁺ or Cr³⁺ ions have excellent persistent luminescence and can potentially be used as advanced luminescent materials (Fu et al., 2021; Yao, 2022). Powder samples of the Ga₄GeO₈ composition were obtained for the first time by solid-phase synthesis (Agafonov et al., 1985). The phase transition α -Ga₄GeO₈ ($C2/m$) \rightarrow β -Ga₄GeO₈ ($P2_1/c$) at temperatures above 1000°C was established by DTA (Agafonov et al., 1985). The structure of the high-temperature modification β -Ga₄GeO₈ belongs to the Fe₃Ge₂O₈ structural type (Kato et al., 1983).

The objectives of this work are: (1) to carry out the synthesis of the Ga₄GeO₈ compound by the hydrothermal method in order to obtain single crystals of the required sizes for further study; (2) refined the structure of the compound by X-ray diffraction; (3) to carry out factor-group analysis of vibrations, as well as *in situ* Raman spectroscopic study at high temperatures.

Synthesis of crystals was carried out under hydrothermal conditions in Cr-Ni ampoules with a volume of 5 ml, lined with platinum, at a temperature of 650°C and a pressure of 100 MPa. A mixture of gallium and germanium oxides in a ratio of 2:1 was used as starting materials. A fluoride solution (4 wt % NH₄F) was poured into an ampoule preliminarily loaded with a mixture of oxides. The ratio of solid phases and solution was 1:1. The pressure was given by the fill factor and estimated from P - V - T diagrams for pure water (Wagner, 2002). The ampoules were sealed, weighed and placed in a Cr-Ni alloy

autoclave containing three ampoules at a time. The autoclave was heated in an electric furnace to 350°C at a rate of 50°C/hour and then to 650°C at a rate of 10°C/hour. The duration of the experiments was 14 days. At the end of the experiment, the autoclaves were quickly (within 1 min) cooled with cold water to prevent the formation of quenching phases. The crystal morphology was studied by optical ADF STD16 and scanning electron (Tescan Vega II XMU) microscopy. For SEM studies, the samples were coated by carbon.

Raman spectroscopy at ambient and high temperatures (up to 600 °C) was carried out using a LabRam HR 800 spectrometer (Horiba Jobin-Yvon, Kyoto, Japan) equipped with a BX-41 microscope (Olympus, Tokyo, Japan) and a THMS600 high-temperature attachment (Linkam, UK). Unpolarized spectra were obtained using a laser with a wavelength of 532 nm, the heating rate was 25 °C/min. It was not possible to study the crystal structure of the obtained sample by single-crystal X-ray diffraction analysis; therefore, the structure was refined by the Rietveld method. To refine the structure, powder patterns were obtained on a RAXIS RAPID II diffractometer with a rotating anode (CoK α radiation, 40 kV, 26 mA). The structure was refined using the Bruker TOPAS v.5.0 software package (Dinnebier et al., 2019).

As a result of the experiments, colorless crystals up to 200 μ m in size were obtained. Gallium germanate was formed as individual crystals, twins, tees, and their intergrowths. The morphology of crystals is characterized by a pseudo-tetragonal habit (Fig. 1).

It was shown by the Rietveld method that the synthesized compound belongs to the structural type Fe₃Ge₂O₈ (sp. gr. $P2_1/c$) with lattice parameters $a = 8.2714(2)$, $b = 8.2402(2)$, $c = 9.0900(2)$ Å, $\beta = 117.676(1)^\circ$, $V = 548.67(2)$ Å³ ($R_{wp} = 2\%$). The crystal structure is based on layers of edge-connected GaO₆ octahedra, which, when connected through GeO₄ and GaO₄ tetrahedra, form a framework. The crystal chemical formula of the compound can be written as Ga₃GaGeO₈. Thus, in this work, a high-temperature modification of β -Ga₄GeO₈ was obtained at 650 °C, which is much lower than the temperature of the previously established phase transition (above 1000 °C). This may be due to the influence of the pressure of 100 MPa created in the autoclave.

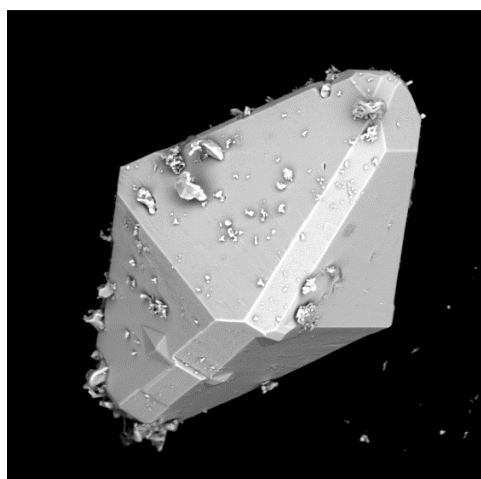


Fig. 1. SEM images of a $\text{Ga}_3\text{GaGeO}_8$ crystal in secondary electrons

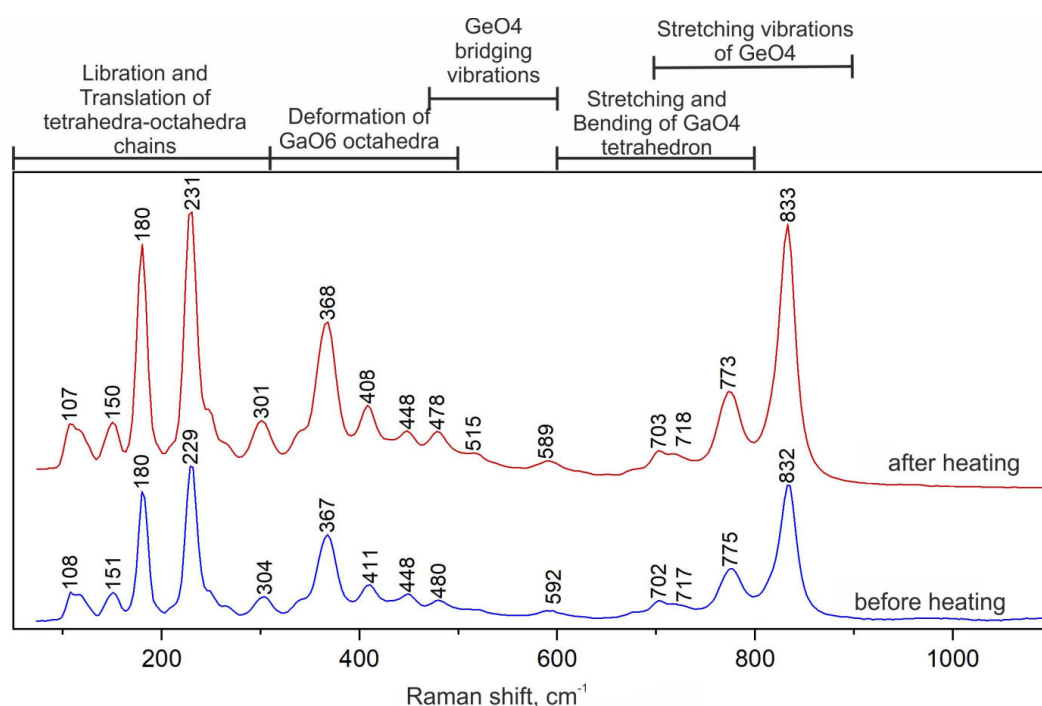


Fig. 2. Raman spectra of the $\beta\text{-Ga}_3\text{GaGeO}_8$ compound at ambient conditions before heating (blue) and after heating (red).

According to the group theory, for a P-cell containing 52 atoms ($Z \cdot 13$ atoms), the number of $3N$ vibrational modes is 156. Removing acoustic modes (for the C_{2h} factor group, this is $A_u, 2B_u$) from the calculation reduces the number of possible vibrations to $\Gamma = 153$.

The Raman spectrum for the compound $\beta\text{-Ga}_3\text{GaGeO}_8$ was obtained in the range of $100\text{--}1100\text{ cm}^{-1}$, in which there are bands of different intensity. Figure 2 shows the Raman spectra under standard conditions with the designation of the main bands. On Figure 3 it is shown the Raman spectra of the $\beta\text{-Ga}_3\text{GaGeO}_8$ compound at temperatures up to $600\text{ }^\circ\text{C}$: as the temperature increases, the spectra monotonically shift to the low-frequency region. In

the region of librational and translational vibrations of chains of tetrahedra-octahedra, the Raman shift was $\square 6\text{ cm}^{-1}$, and in the region of bending vibrations of GaO_6 octahedra and bending and stretching vibrations of GeO_4 and GaO_4 tetrahedra, $\square 12\text{ cm}^{-1}$. As a result of the analysis of changes in the Raman spectra with an increase in temperature up to $600\text{ }^\circ\text{C}$, it was shown that there are no polymorphic transitions in the studied temperature range. After completion of heating and subsequent cooling, the Raman spectrum of $\beta\text{-Ga}_3\text{GaGeO}_8$ almost completely repeats the initial spectrum at ambient conditions with a slight shift of the main bands by $1\text{--}3\text{ cm}^{-1}$ (Fig. 2).

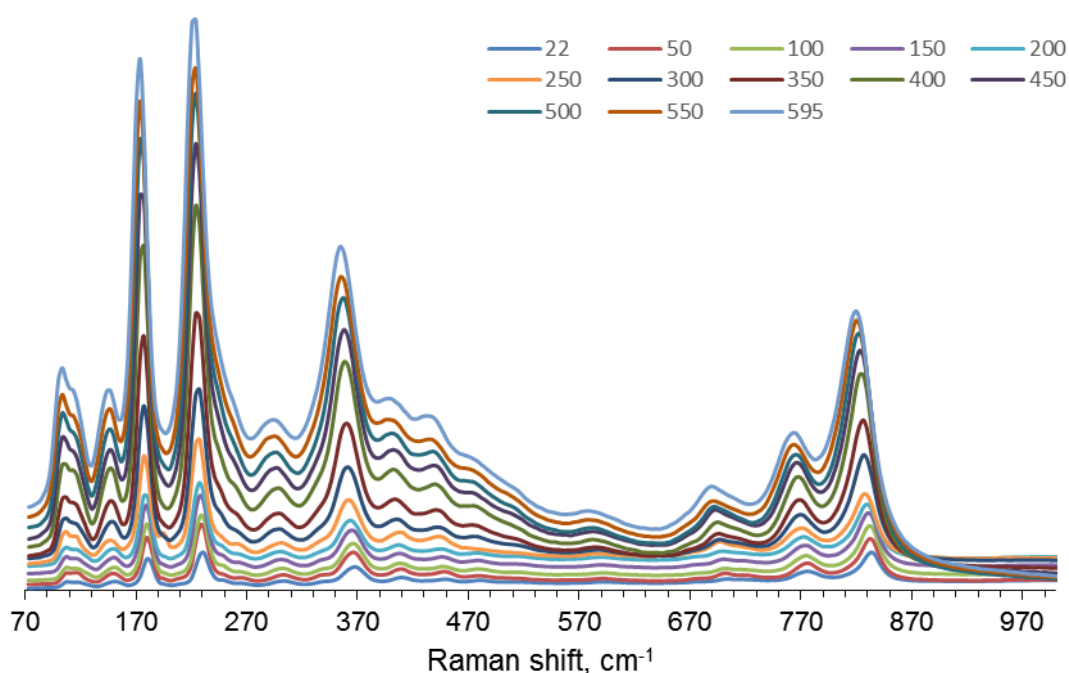


Fig. 3. Raman spectra of the β -Ga₃GaGeO₈ compound at various temperatures up to 600°C.

As a result of the work, single crystals of the compound β -Ga₃GaGeO₈ with a size of up to 200 μ m were obtained at 650 °C and 100 MPa under hydrothermal conditions. The chemical composition was determined and the structural characteristics of the synthesized crystals were established. A factor-group analysis of vibrations has been carried out. The existence of 153 possible of active Raman vibrations has been established. Raman spectra of the β -Ga₃GaGeO₈ compound were obtained for the first time at ambient conditions, as well as at elevated temperatures up to 600°C. The shift of the main bands of the spectrum to the region of low frequencies with increasing temperature was shown. No polymorphic transitions were found in the studied temperature range.

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This study is fulfilled under Research program № FMUF-2022-0002 of the Korzhinskii Institute of Experimental Mineralogy.

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