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Abstract

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On the Low-Temperature Hexagonal Modification of $NaYF_4$ with the Gagarinite Structure

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The question of the structure of the low-temperature modification of the compound with the stoichiometric formula $NaF \cdot YF_3 = NaYF_4$ has until recently remained open. There are indications ([3], [4]) that upon annealing and synthesis of the high-temperature modification $NaYF_4$, which has the fluorite structure, a phase is obtained whose powder X-ray pattern cannot be indexed on the basis of a cubic cell. More detailed data on the structure of $NaYF_4$ are not given.

For the purpose of further study of the compound $NaYF_4$, the latter was obtained by us by two methods.

Table 1

Results of the calculation of the powder X-ray pattern of synthetic β-$NaYF_4$ and gagarinite

I	d	hkl	$1/d^2$ found	$1/d^2$ calc.	I	d	hkl
7	5,15	100	0,0378	0,0377	4	5,153	100
8	2,970	110	0,1134	0,1130	7	2,980	110
9	2,902	101	0,1187	0,1183	5	2,914	101
1,7	2,574	200	0,1509	0,1507	2	2,587	200
1	2,501	–	0,1599	–	–	–	–
3,6	2,270	111	0,1941	0,1936	4 .	2,291	111
10	2,079	201	0,2314	0,2313	9	2,085	201
2	1,947	210	0,2638	0,2637	4	1,953	210
2	1,756	002	0,3236	0,3223	3	1,766	002
4,5	1,718	301	0,3388	0,3390	9	1,726	301
7,3	1,704	211	0,3444	0,3443	10	1,709	211
1,3	1,663	102	0,3616	0,3600	2	1,673	102
1,2	1,515	112	0,4357	0,4354	3	1,519	112
1,1	1,488	220	0,4516	0,4520	5	1,495	220
0,6	1,459	202	0,4698	0,4734	2 .	1,462	202
0,6	1,451	–	0,4750	0,4730	2 .	1,462	202
0,6	1,429	310	0,4897	0,4897	3	1,436	310
0,5	1,355	–	0,5447	–	1	1,361	221

Figure 1

Figure 1: Figure 1

I	d	hkl	$1/d^2$ found	$1/d^2$ calc.	I	d	hkl
1,7	1,326	311	0,5687	0,5693	6	1,330	311
1,1	1,307	212	0,5854	0,5860	4	1,313	212
–	–	–	–	–	2	1,295	400
0,5	1,236	–	0,6546	–	–	–	–
2,1	1,231	302	0,6599	0,6613	6	1,235	302
0,5	1,211	401	0,6819	0,6805	2	1,218	401
0,5	1,184	320	0,7133	0,7157	2	1,191	320
0,7	1,144	103	0,7641	0,7629	2	1,152	103
1	1,137	222	0,7735	0,7440	3	1,143	222
1,7	1,126	–	0,7887	–	–	–	–
3,1	1,123	410	0,7930	0,7911	10 .	1,129	(410;321)
1,8	1,118	–	0,8000	–	–	–	–

Fig. 1. Diffraction patterns: *a* –product of hydrothermal recrystallization at 500° (49 h) of the alloy $NaYF_4$; *b* –product of hydrothermal synthesis from NaF and Y_2O_3 at 500° (18 h); *c* –natural gagarinite $Na(CaY)F_6$. Recording conditions: URS-50I, Fe anode, b/f, 7 mA, 25 kV.

1) By recrystallization of a melt of stoichiometric composition $NaYF_4$ under hydrothermal conditions at a temperature below the transition to the $\alpha \rightarrow \beta$ modification. As we were able to verify, this method is much more effective than annealing, especially at such temperatures as 500° (the upper limit was set by the temperature of the $\alpha \rightarrow \beta$ transition).

2) By synthesis of $NaYF_4$ under hydrothermal conditions from sodium fluoride and yttrium oxide (molar ratio in the mixture $Na : Y = 1 : 1$). To fluorinate the yttrium oxide, the autoclave was filled with a 10% solution of hydrofluoric acid (degree of filling 0.3). The duration of the experiments was 18 h at 500°.

Identification of the products obtained under the above conditions was carried out by X-ray and chemical analyses. The X-ray study was performed on a URS-50I diffractometer. Fe K_α radiation was used; reflection recording from flat specimens; recording conditions 7 mA at 25 kV. Lines belonging to β-radiation were filtered out after measurement and are not included in the tables. In addition, powder patterns were obtained with an RKD-57 camera, copper radiation, Ni filter.

Table 2

Chemical analysis of the synthesis product*

Fig. 2. Heating curves: a–synthesized $Na(Y_{1\ 5}Na_{0\ 5})F_6$; b–natural gagarinite $Na(YCa)F_6$

Figure 2: Fig. 2. Heating curves: a–synthesized $Na(Y_{1\ 5}Na_{0\ 5})F_6$; b–natural gagarinite $Na(YCa)F_6$

Components	Wt. %	Atomic amounts of cations and F	Atomic amounts of cations and F	Relative atomic amount
Na_2O	17.27	0.5570	0.5570	1.04
CaO	0.50	0.0089	0.5356	1.00
FeO	1.06	0.0147	0.5356	1.00
Y_2O_3	57.85	0.5120	0.5356	1.00
F	40.30	2.1211	2.1211	3.96
Σ	116.98			
$O = F_2$	16.93			
Sum	100.05			

* Analyst A. V. Bykova.

The results of the X-ray investigation are given in Table 1 and in Fig. 1. The products obtained by both the first and the second methods proved to be completely identical and have a structure sharply different from the high-temperature (fluorite) α-$NaYF_4$ modification.

Recalculation of the analytical results given in Table 2 gives the formula

$$Na_{1.04}(Y_{0.95}Fe^{2+}_{0.03}Ca_{0.02})_{1.00}F_{3.96} \quad \text{or} \quad NaYF_4.$$

Analyzing the X-ray data for β-$NaYF_4$ presented above, we came to the conclusion that they coincide completely with the X-ray characteristics of gagarinite–a recently discovered mineral with the formula $Na(YCa)F_6$ ([1], [2]). This similarity follows from the diffractograms shown in Fig. 1, and is also clearly observed in comparison of ordinary powder X-ray patterns. To determine the unit-cell parameters of β-$NaYF_4$, we indexed the powder pattern of this compound (see Table 1). The lattice parameter c proved to be equal to the corresponding value for natural gagarinite, while the parameter a is somewhat smaller.

Fig. 2. Heating curves: *a*–synthesized $Na(Y_{1\ 5}Na_{0\ 5})F_6$; *b*–natural gagarinite $Na(YCa)F_6$.

Thus, we have shown that the low-temperature modification β-$NaYF_4$ crystallizes in the gagarinite structure with parameters of the hexagonal unit cell $a_0 = 5.96$ Å, $c_0 = 3.53$ Å. For natural gagarinite, we have ([1]) $a = 5.99$ Å, $c = 3.53$ Å.

The calculation of the number of molecules per unit cell (based on the composition $NaYF_4$ and taking the density of the low-temperature modification of this compound to be 4.23 g/cm^3 ([3])) gives 1.47 formula units. This value corresponds to the gross formula $Na_{1.5}Y_{1.5}F_6$, i.e., to the stoichiometry of gagarinite, $Na(YCa)F_6$. Taking into account the crystallochemical studies of the latter ([2]), the formula $NaYF_4$ should be written in the form $Na(Y_{1.5}Na_{0.5})F_6$. Such a notation will fully reflect the crystallochemical features of the β-modification of this compound.

To determine the temperature of the $\beta \rightarrow \alpha$ modification transition, we carried out thermographic analysis of the synthesized samples. The heating curve of one of them is shown in Fig. 2. The endothermic effect at 670° (temperature measured from the onset of the effect) corresponds to the transition of the hexagonal modification into the cubic one. A similar effect on the heating curve of natural gagarinite begins at a temperature of 685°. The reverse transition ($\alpha \rightarrow \beta$) is considerably hindered, as a result of which the β-modification can be obtained only by prolonged annealing.

X-ray diffraction studies of the product heated above 670° showed that it indeed has the fluorite structure indicated earlier for the α-modification $Na(Y_{1.5}Na_{0.5})F_6$ ([4]).

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Note: Figure translations are in progress. See original paper for figures.