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New phases of K, Eu-silicate in the family of compounds with the orthorhombic pellyite-like unit cell

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The structures of three phases of the synthesized europium potassium silicate were determined by X-ray diffraction. Two of these phases crystallize in a new structural type. The chemical formulas of the phases were determined. The orthorhombic unit-cell parameters of all three phases are equal: $a = 14.852(1)$ Å, $b = 15.902(1)$ Å, $c = 7.243(1)$ Å, sp. gr. $P2_12_12$ (phase **I**) and sp. gr. *Pbam* (phases **II** and **III**). The structures were solved by direct methods and refined from X-ray diffraction data collected from one crystal to $R = 0.0271$, 0.0479, and 0.0582 based on 4370, 3320, and 2498 reflections, respectively, with $|F| > 3\sigma(F)$. The crystalchemical formulas of the phases (Z=4) are $K_3Eu^{3+}[Si_6O_{15}]$. $2H_2O$, $K_3Eu^{3+}[Si_6O_{13}(OH)_4]$. $2H_2O$, and $K_3Eu^{3+}[Si_4O_{9.5}(OH)](OH)_2$. $5.5H_2O$. The structure of phase **I** consists of silicon–oxygen sheets $[Si_6O_{15}]$ analogous to those found in the isostructural compound $K_3Nd[Si_6O_{15}] \cdot 2H_2O$. In the structures of phases **II** and **III**, the ribbons $[Si_6O_{17}]$ and $[Si_8O_{21}]$ run along the shortest c axis and are linked together by Eu^{3+} octahedra and trigonal prisms to form three-dimensional layered and framework structures containing K atoms between the sheets and in the channels.

Key words: europium potassium silicate, X-ray diffraction, crystal structure, crystal chemistry, endotaxy.

INTRODUCTION

Eu-containing potassium and sodium silicates are of interest because of photoluminescence, ion-exchange and some other properties of these microporous compounds. The crystals were synthesized at the Vinogradov Institute of Geochemistry and Analytical Chemistry, Siberian Division, Russian Academy of Sciences, by a research group headed by V.L. Tauson. The hydrothermal synthesis of Eu-containing phases was carried out from a mixture of silicon, aluminum, and europium oxides under a total pressure of 1000 atm and temperature 500 °C during 45 days in autoclaves [1]. The colorless transparent crystals were synthesized as rhombic prisms up to 1.5 mm in length. The chemical composition of the phases was determined on a JXA-8200 electron probe X-ray microanalyzer and the nonstoichiometrycal formula calculated for six Si atoms is $Eu_{0.84}Al_{0.03}Si_6K_{1.98}O_{14.31}$.

Here we report on study by X-ray diffraction of Eu-containing phases. Two crystals were studied, and three different phases having the pellyite unit cell were found in each crystal. The simultaneous presence of several phases in the same crystal has not been structurally studied previously.

EXPERIMENTAL

The X-ray diffraction data collected from two crystals within a full sphere of reciprocal space on an Oxford Diffraction Xcalibur diffractometer equipped with a CCD detector are presented in Table 1. Data sets contain averaged 4805 and 4477 $|F|>3\sigma(F)$ respectively. An analysis of the systematic absences suggested sp. grs. *Pbam* and $P2_12_12$. It should be noted that five weak reflections $0kl$ with $k \neq 2n$ and $h0l$ with $h \neq 2n$ were inconsistent with sp.gr. *Pbam*.

It was found that the X-ray diffraction patterns of both crystals of europium potassium silicate are superimpositions of three individual phases. Structural investigation of these phases was a challenging task taking into account that it was impossible to separate the contributions of the three components in overlapping reflections, which made it difficult to localize oxygen atoms belonging to water molecules and resulted in high R factors, particularly for the third phase. Inspection of reciprocal diffraction space demonstrated that there were no additional satellite reflections or diffuse streaks be-

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Table 1. Crystallographic characteristics and X-ray data-collection statistics

Crystal samples	1	2
a, Å	14.852(1)	14.858(1)
b, Å	15.902(1)	15.890(1)
c, Å	7.243(1)	7.245(1)
V, Å^3	1710.60(3)	1710.49(3)
Diffractometer	Xcalibur Oxford Diffraction, CCD detector	
Radiation, λ, Å	MoK$_\alpha$; 0.71073	
Scan mod	ω	
θ_{max}, deg	55.01	54.95
h, k, l ranges	$-34<h<29$, $-35<k<31$, $-16<l<16$	$-29<h<32$, $-34<k<34$, $-16<l<16$
Crystal dimensions, mm	0.20×0.25×0.27	0.25×0.25×0.5
Number of measured / independent reflections	15038 $\|F\|>3\sigma(F)$ / 4805 $\|F\|>3\sigma(F)$	14371 $\|F\|>3\sigma(F)$ / 4477 $\|F\|>3\sigma(F)$
R_{int}	0.016	0.020
Computational program	AREN [2,3]	
Program for absorption correction	DIFABS [4]	

tween main reflections which were the evidence of the zonal structure of crystals or modulation nature of cation distribution.

The translation lattices of all phases are described by an orthorhombic unit cell parameters a = 14.852(1) Å, b =15.902(1) Å, c = 7.243(1) Å, sp. gr. $P2_12_12$ (phase **I**) and sp. gr. *Pbam* (phases **II** and **III**). The most reflections (~95%) took part in the indexing in the frame of these cell parameters. The strongest reflections corresponding to fragments of the sublattice formed by europium, potassium, and part of the silicon atoms are common to the three structures. Independent reflections are individual and were included in the least-squares refinement of each component, whereas the remaining reflections were rejected based on the residual. The maximum number of reflections (~90%) belongs to phase **I**, and the minimum number of reflections (~50%) belongs to phase **III**. For phase **II**, ~70% of the total number of reflections was used. In crystal 2 the ratio of the phases is the same, whereas the intensities of reflections belonging to phases **II** and **III** are redistributed in accordance with their volumes. Thus, the volume of phase **III** in crystal 2 is larger. This allowed us to obtain the structural model of phase **III** by direct methods, whereas the model of phase **II** was found by direct methods only with the use of the experimental data collected from crystal 1.

The crystal structures of all three phases were found by direct methods with following the automatic successive approximation procedure [2, 3]. Some water molecules were found from the difference electron density map. All three structures refined with the use of the same X-ray diffraction data set collected from crystal 1 (Table 2). All calculations were carried out with the use of the AREN program package [2,3]. The absorption correction was applied using the DIFABS program [4].

Table 2. Some crystal-structural data for three phases (all structures were refined with the use of the X-ray diffraction data set collection from crystal 1)

Phases	I	II	III
Chemical formula (Z=4)	$K_3Eu^{3+}[Si_6O_{15}]\cdot 2H_2O$	$K_3Eu^{3+}[Si_6O_{13}(OH)_4]\cdot 2H_2O$	$K_3Eu^{3+}[Si_4O_{9.5}(OH)](OH)_2\cdot 5.5H_2O$
Sp. gr., Z	$P2_12_12$, 4	*Pbam*, 4	*Pbam*, 4
Number of independent reflections	4370 $\|F\|>3\sigma(F)$	3320 $\|F\|>3\sigma(F)$	2498 $\|F\|>3\sigma(F)$
Density ρ_{calc}, g/cm^3	2.771	2.911	2.654
R factor upon isotropic/ anisotropic refinement	7.06 / 2.71	7.86 / 4.79	12.73 / 5.82

Table 3. Atomic coordinates and equivalent isotropic displacement parameters (B_{eq}) for structure of phase I

Atom	*x*	*y*	*z*	B_{eq}, Å^2
Eu1	0	0	–0.0034(1)	0.59(2)
Eu2	0	0.5	0.0000(1)	0.77(1)
K1	0.0890(1)	0.4295(1)	0.490(1)	3.61(4)
K2	0.3422(1)	0.3445(1)	0.504(1)	4.16(3)
K3	0.1162(1)	0.2132(1)	1.027(1)	4.92(4)
Si1	0.2001(1)	0.0380(1)	0.7199(1)	0.68(5)
Si2	0.3665(1)	0.1452(1)	0.2861(1)	0.51(5)
Si3	0.3729(1)	0.2908(1)	0.002(1)	0.56(4)
Si4	0.3643(1)	0.1440(1)	0.7157(2)	0.88(5)
Si5	0.2182(1)	0.4093(1)	–0.001(1)	0.78(4)
Si6	0.2001(1)	0.0374(1)	0.2829(2)	0.97(5)
O1	0.2666(2)	0.3170(1)	0.002(2)	1.5(2)
O2	0.4404(1)	0.3678(1)	0.001(2)	1.2(2)
O3	0.4323(2)	0.0696(2)	0.243(1)	1.5(2)
O4	0.1124(2)	0.3982(2)	0.002(2)	1.8(2)
O5	0.0999(2)	0.0500(3)	0.221(1)	1.7(2)
O6	0.3885(2)	0.2317(2)	0.177(1)	1.3(2)
O7	0.3882(3)	0.2333(3)	0.814(1)	1.9(2)
O8	0.2555(3)	0.4573(2)	0.180(1)	2.0(2)
O9	0.2105(2)	0.0154(2)	0.505(2)	1.6(2)
O10	0.0984(3)	0.0528(3)	0.781(1)	1.9(2)
O11	0.2592(2)	0.1217(2)	0.759(1)	1.1(2)
O12	0.3692(2)	0.1734(2)	0.502(1)	1.6(2)
O13	0.2614(3)	0.1224(3)	0.238(1)	1.7(2)
O14	0.4315(3)	0.0706(3)	0.757(1)	1.9(2)
O15	0.2518(3)	0.4559(3)	0.812(1)	1.9(2)
W(1)	0.014(1)	0.132(1)	0.496(3)	6.3(2)
W(2)	0.164(1)	0.270(1)	0.417(2)	6.8(1)

Because of the lack of precise chemical data, the atomic positions in the models were identified based on the crystal-chemical criteria. The H_2O molecules and OH-groups were revealed by the bond-valence method according to Brese [5]. Atomic coordinates and equivalent isotropic displacement parameters (B_{eq}) for the structures are given in Tables 3–5.

The Eu atoms are in special positions 00 *z* and 0 0.5 *z* and have an octahedral or trigonal-prismatic coordination with average bond lengths ranging from 2.31 to 2.32 Å (Table 6), which confirm there trivalent state. As a result, we determined the chemical and crystal-chemical formulas of the three individual phases.

STRUCTURES DESCRIPTION

Figure 1 shows the silicon–oxygen groups, which were found in the structures of the three phases and pellyite. The full structures of the phases I-III and pellyite are presented in Figs. 2–5.

Phase I

The structure of phase **I** was solved with the use of the X-ray diffraction data, which were collected from crystal 1 and merged in sp. gr. $P2_12_12$. Atomic coordinates and equivalent isotropic displacement parameters (B_{eq}) for this structure are given in Table 3. The Eu atoms are in special positions 00 *z* and 0 0.5 *z* and have an octahedral coordination with bond lengths ranging from 2.280(2) to 2.340(4) Å (Table 6). The Si atoms are in tetrahedral sites surrounded by O atoms with the following bond lengths: Si1–O = 1.589(5)–1.618(3) Å; Si2–O = 1.580(4)–1.620(4) Å; Si3–O = 1.583(2) –1.656(6) Å; Si4–O = 1.564(5)–1.631(3) Å; Si5–O = 1.581(3)–1.634(3) Å; and Si6–O = 1.566(3)–1.662(5) Å. The tetrahedra are linked together to form diortho groups, which are arranged perpendicular to each other in a chess-board fashion and are linked together by shared vertices to form corrugated silicon–oxygen sheets containing loops of three types (eight-, six-, and four-membered) (Fig. 1a). The sili-

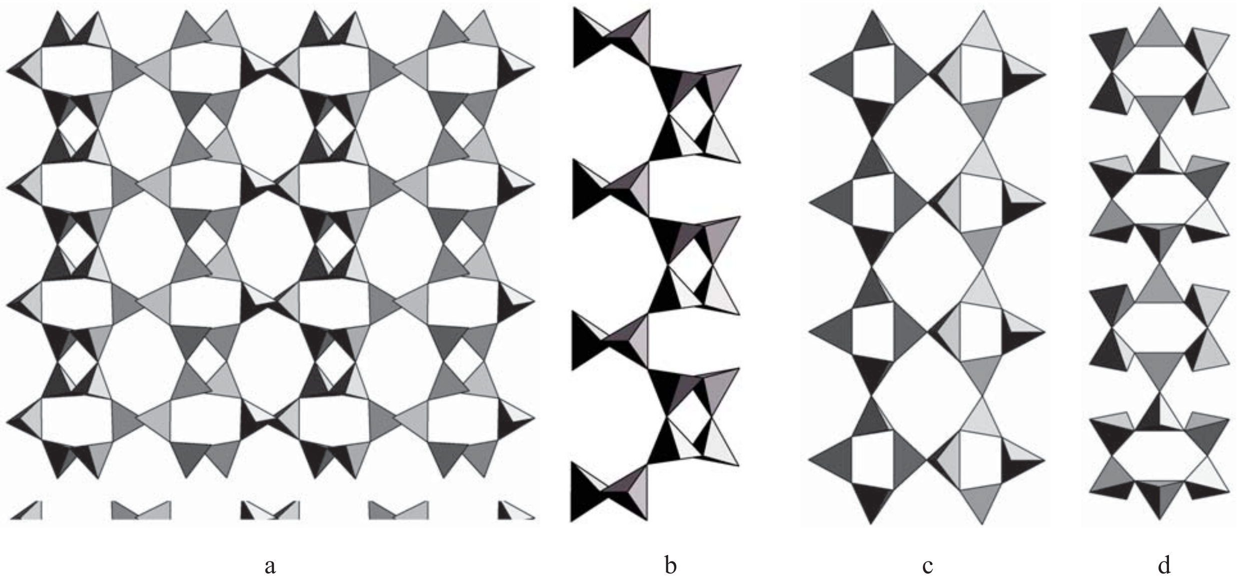

Fig. 1. Silicon–oxygen sheet [Si_6O_{15}] in the structure of phase **I** (a); silicon–oxygen ribbon [Si_6O_{17}] in the structure of phase **II** (b); the ribbon [Si_8O_{21}] in the structure of phase **III** (c) and [Si_6O_{17}] in the structure of pellyite (d)

con sheets are linked together by the europium octahedra to form a mixed framework structure. The latter contains channels running along the shortest period (~7 Å) which are occupied by potassium atoms and water molecules coordinated to potassium (Fig. 2). A similar structural type has been found previously in the compound $K_3Nd[Si_6O_{15}].2H_2O$ [6, 7] with the symmetry described by the sp. gr. *Pbam* in both publications. Although the structural motif of the K,Nd-containing compound is identical to that of the Eu-containing compound, the symmetry of the latter is reduced to $P2_12_12$ due to the displacement of some atoms from the symmetry plane *m*.

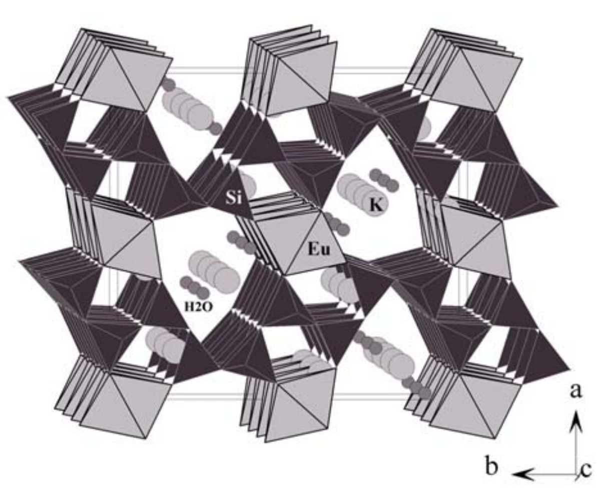

Fig. 2. Crystal structure of phase I

The chemical formula of phase I found from the X-ray diffraction data is (for Z=4): $K_3Eu^{3+}[Si_6O_{15}] \cdot 2H_2O$.

Phase II

Atomic coordinates and equivalent isotropic displacement parameters (B_{eq}) for phase II structure are given in Table 4. The principal compositional and structural characteristics of phase **II** are reflected in its crystal chemical formula (Z = 4) $Eu^{3+}K_3[Si_6O_{13}(OH)_4]$. $2H_2O$. The Eu atoms occupy special positions *xy*0 ($x \sim 0$, $y \sim 0.25$) and are in an octahedral environment with the Eu–O bond lengths ranging from 2.298(7) to 2.322(6) Å (Table 6). Four independent Si atoms are in tetrahedral sites surrounded by O atoms with the following Si–O bond lengths: Si1–O = 1.571(5)–1.77(1) Å; Si2–O = 1.578(5)–1.632(2) Å; Si3–O = 1.587(7)–1.633(6) Å, and Si4–O = 1.560(7)–1.76(1) Å. The Si tetrahedra are linked together to form diortho groups, which form corrugated ribbons of a new type running along the shortest *c* axis. In spite of the fact that the ribbons have a [Si_6O_{17}] composition identical to that found in pellyite, these ribbons are topologically different (Fig. 1b, 1d). The asymmetric ribbons of phase **II** are cutouts of the above-described layer. The ribbons are arranged parallel to each other and are linked together by discrete Eu octahedra to form mixed sheets perpendicular to the longest period (~16 Å). The K atoms and water molecules involved in the coordination environment of K are located between the sheets and in channels

Table 4. Atomic coordinates and equivalent isotropic displacement parameters (B_{eq}) for structure of phase II

Atom	x	y	z	B_{eq}, Å^2
Eu	–0.0006(1)	0.2510(1)	0	0.66(1)
K1	0.3711(4)	0.4243(3)	0.5	4.02(3)
K2	0.3441(3)	0.0939(2)	0.5	3.52(3)
K3	0.1463(4)	0.1934(4)	0.5	6.12(3)
Si1	0.1346(1)	0.3947(1)	0.2854(2)	0.70(4)
Si2	0.2999(1)	0.2877(1)	0.2816(2)	0.84(4)
Si3	0.2817(1)	0.1593(1)	0	0.81(6)
Si4	0.1262(1)	0.0411(1)	0	0.45(6)
O1	0.2330(4)	0.0672(3)	0	1.4(3)
O2	0.289(1)	0.264(1)	0.5	1.5(3)
O3	0.388(4)	0.1486(4)	0	1.8(2)
O4	0.252(1)	0.2066(3)	0.185(1)	2.0(1)
O5	0.248(1)	0.3731(3)	0.240(1)	2.4(2)
O6	0.0688(4)	0.3201(3)	0.231(1)	1.7(2)
O7	0.0593(4)	0.1168(4)	0	1.3(2)
O8	0.4006(3)	0.3022(4)	0.219(1)	1.8(2)
O9	0.191(1)	0.405(1)	0.5	9.1(1)
OH1	0.379(1)	0.476(1)	0.198(2)	5.40(8)
OH2	0.1088(4)	0.4819(4)	0.179(1)	1.8(2)
W(1)	0.024(1)	0.104(1)	0.5	4.3(1)
W(2)	0.484(2)	0.173(2)	0.5	6.5(1)

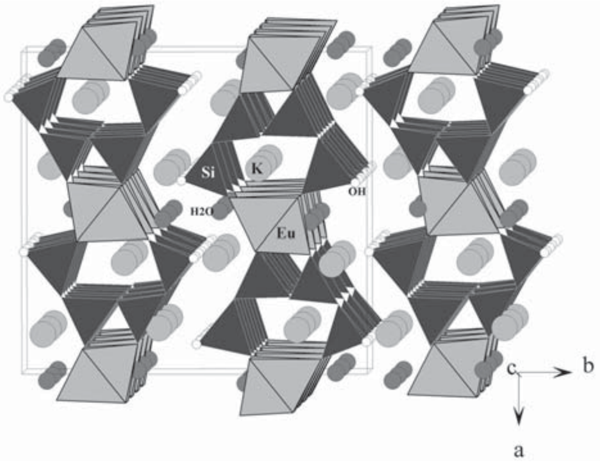

Fig. 3. Crystal structure of phase II

inside the ribbons (Fig. 3). The mixed sheets are also linked by hydrogen bonds between OH groups and water molecules to form a three-dimensional structure.

Phase III

Atomic coordinates and equivalent isotropic displacement parameters (B_{eq}) for the phase III structure are given in Table 5. The principal compositional and structural characteristics of the mineral are reflected in its crystal-chemical formula ($Z = 4$): $K_3Eu^{3+}[Si_4O_{9.5}(OH)](OH)_2$. $5.5H_2O$. The europium atoms in phase **III**, like those in phase **II**, are in special positions $xy0$ ($x \sim 0.25$, $y \sim 0$) with the Eu–O bond lengths ranging from 2.30(1) to 2.32(1) Å (Table 6). This phase differs from the other two phases in that the Eu octahedron is transformed into a trigonal prism. Two vertices of the prism are occupied by OH-groups.The Si atoms are in tetrahedral sites surrounded by O atoms with the following Si–O bond lengths: Si1–O = 1.55(1)–1.68(1) Å; Si2–O =1.569(8)–1.65(1) Å; and Si3–O = 1.523(3)–1.74(1) Å. The tetrahedra are linked together to form strongly corrugated silicon–oxygen ribbons of a new type. It should be noted that the ribbons in phase **II** are exact cutouts of the sheet, whereas the configuration of the ribbon in phase **III** only partially corresponds to the sheet and inherits the fragment of eight-membered rings. The ribbon formed as a result of this transformation is unique (Fig. 1c). The ribbons are parallel to the short *c* axis and are arranged in a chess-board fashion along the diagonals of the (001) plane. The Eu trigonal prisms are located between the silicon ribbons and link the latter to form a mixed framework structure whose channels are occupied by two types of potassium polyhedra with eight and nine vertices, respectively (Fig. 4).

Table 5. Atomic coordinates and equivalent isotropic displacement parameters (B_{eq}) for structure of phase III

Atom	*x*	*y*	*z*	B_{eq}, Å^2
Eu	0.2490(1)	–0.0002(1)	0	0.79(1)
K1	0.1321(1)	0.2880(1)	0	1.56(4)
K2	0.1663(2)	0.0676(2)	0.5	2.22(4)
K3	0.4051(2)	0.1563(2)	0.5	2.31(4)
Si1	0.3812(2)	0.2062(2)	0	1.17(7)
Si2	0.3842(1)	0.3553(1)	0.2853(3)	0.88(5)
Si3	0.0323(2)	0.0909(2)	0	1.00(1)
O1	0.377(1)	0.325(1)	0.5	1.6(3)
O2	0.139(1)	0.102(1)	0	1.9(3)
O3	0.361(1)	0.267(1)	0.186(1)	1.9(2)
O4	0.317(1)	0.430(1)	0.245(1)	1.7(2)
O5	0.488(1)	0.375(1)	0.230(1)	2.3(2)
O6	0.5	0.5	0	4.8(3)
O7	0.314(1)	0.132(1)	0	1.7(3)
OH1	0.485(1)	0.183(1)	0	1.6(3)
OH2	0.149(1)	0.450(1)	0.217(1)	1.9(28)
*W*1	0.099(1)	0.227(1)	0.5	2.8(3)
*W*2	0.019(1)	0.381(1)	0.259(2)	3.3(2)
*W*3	0	0.5	0.5	5.3(3)
*W*4	0.240(1)	0.206(1)	0.5	4.4(2)

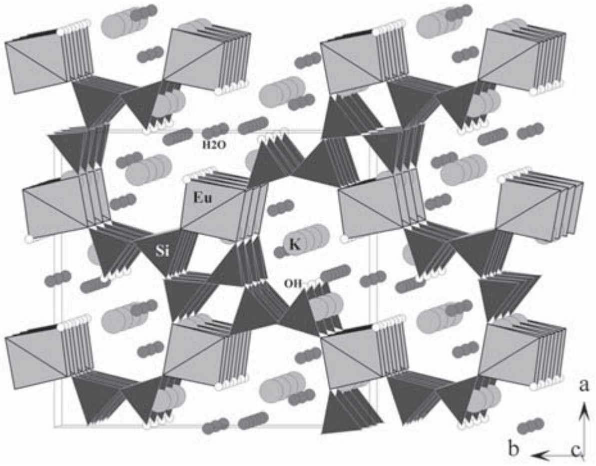

Fig. 4. Crystal structure of phase III

DISCUSSION

The epitaxy, or the oriented growth of one crystal on another, resulting in the coherent intergrowth of two lattices is the most commonly observed process. The topotaxy or syntaxy are also described as intergrowths of phases but within the same crystal. We studied by X-ray diffraction the topotaxy of natural Ba,Mn-titanosilicate [8] because it was possible to separate the reflections belonging to each of two mineral modifications with the axes of their unit cells turned at an angle of 60°.

The phenomenon observed in this study can be assigned to endotaxy, as the oriented growth of one crystal inside another. Endotaxy appears in crystals because all the three phases with equal unit cell parameters, similar symmetry, chemically

Table 6. Selected bond lengths (Å) in the structure of phases I, II, III

Phase-I				Phase-II		Phase-III	
Eu1-O2	2.280(2)x2	Eu2-O3	2.310(4)x2	Eu-O3	2.298(7)	Eu-O2	2.30(1)
Eu1-O10	2.300(5)x2	Eu2-O14	2.322(5)x2	Eu-O6	2.302(6)x2	Eu-O7	2.30(1)
Eu1-O5	2.340(4)x2	Eu2-O4	2.324(5)x2	Eu-O7	2.312(6)	Eu-O4	2.317(7)x2
				Eu-O8	2.322(6)x2	Eu-OH2	2.320(9)x2
average	2.307	average	2.319	average	2.310	average	2.312

Table 7. Crystalstructural data for the family of compounds with the orthorhombic pellyitelike unit cell and related Si,O-radicals

Formula	Si,O-radicals	Unit cell dimensions, Å	Space group	References
$K_3Nd[Si_6O_{15}]?2H_2O$	$[Si_6O_{15}]_{??}$	*a*=16.008(2) *b*=15.004(2) *c*=7.2794(7)	*Pbam*	[6,7,9]
$K_3Nd[Si_6O_{15}]$	$[Si_6O_{15}]_{??}$	*a*=14.370(2) *b*=15.518(2) *c*=14.265(2)	$Bb2_1m$	
$Cs_2Th[Si_6O_{15}]$	$[Si_6O_{15}]_{??}$	*a*=16.2920(10) *b*=7.2154(6) *c*=13.6800(10)	$Pca2_1$	[10]
$K_3Eu^{3+}[Si_6O_{15}]\cdot 2H_2O$	$[Si_6O_{15}]_{??}$	*a*=14.852(1), *b*=15.902(1), *c*=7.243(1)	$P2_12_12$	[1, present study]
$K_3Eu^{3+}[Si_6O_{13}(OH)_4]\cdot 2H_2O$	$[Si_6O_{17}]_?$		*Pbam*	
$K_3Eu^{3+}[Si_4O_{9.5}(OH)](OH)_2\cdot 5.5H_2O$	$[Si_8O_{21}]_?$			
$Ba_3CaCu[Si_6O_{17}]$	$[Si_6O_{17}]_?$	*a*=14.405(2) *b*=16.077(2) *c*=7.088(2)	*B2mb*	[11]
Pellyite $Ba_2CaFe^{2+}{}_2[Si_6O_{17}]$	$[Si_6O_{17}]_?$	*a*=15.677(4) *b*=7.15(2) *c*=14.209(6)	*Cmcm*	[12]

and structurally related and coherently oriented. As it has been shown previously, these three phases crystallize in sp. gr. *Pbam* and its lower subgroup $P2_12_12$; they have identical europium and potassium sublattices; and both silicon–oxygen ribbons are cutouts of the same silicon–oxygen sheet. The presence of these phases in the crystals under study is, apparently, attributed to the specific crystallization conditions. Thus, nonequilibrium crystal growth for 45 days is accompanied by the fractionation of chemical elements due to the formation of additional compounds. The true volumes of these phases are unknown. However, it can be suggested that phase **I** containing the silicon–oxygen sheet dominates over the other two phases in both crystals; phase **II** containing $[Si_6O_{17}]$ ribbons dominates over phase **III** consisting of $[Si_8O_{21}]$ ribbons in crystal 1; and, on the contrary, phases **I** and **III** are the largest components in crystal 2. The difference in the volumes of the three phases is indirectly confirmed by the fact that these phases are characterized by different intensities of the corresponding reflections in the experimental data collected from two crystals.

Eight synthetic compounds and natural mineral with orthorhombic pellyite-like unit-cell are summarized in Table 7. The base of their structures is formed by cations with close ionic-radii: Ca (1.00 Å), Eu^{3+} (0.95 Å), Nd^{3+} (0.98 Å), Th^{4+} (0.94 Å). Their special positions led to the parameters of orthorhombic unit-cells which vary in the range of *a*=15.52–16.29 (av. 15.9) Å, *b*=13.68–15.00 (av. 14.34) Å, *c*=7.1–7.28 (av. 7.19) Å. These variations are related to the presence of large cations K, Ba, Cs and water molecules in the channels of the structures, as well as additional small cations Fe^{2+} in pellyite and Cu in its synthetic analog.

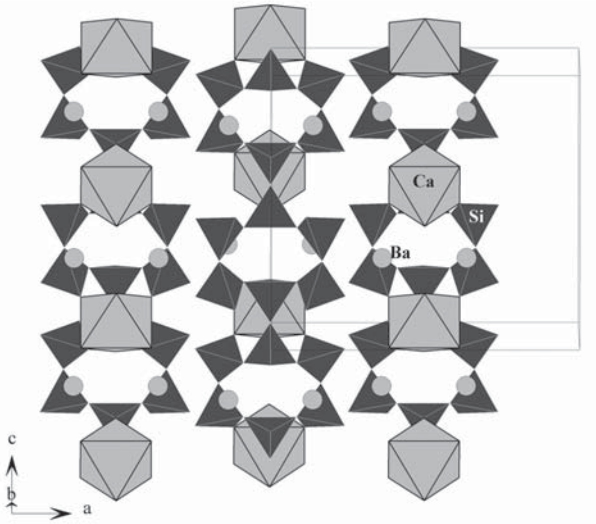

Fig. 5. Crystal structure of pellyite. Fe tetrahedra are not shown

These representatives have different Si,O radicals related to the $[Si_6O_{15}]$ sheet which was found in four structures. Among other structures three have $[Si_6O_{17}]$ ribbons (including two pellyitelike bands) and one $[Si_8O_{21}]$ which are cutouts from the sheet and two of them present unknown for to-day Si,O-radicals. The bands $[Si_6O_{17}]$ in the pellyitelike structures (Fig. 5) are also cutouts from the sheet but in transverse direction.

CONCLUSIONS

To sum up, the structure solution and refinement of three phases showed the presence of endotaxic (or syntaxic) intergrowths in crystals of synthetic europium potassium silicate having a orthorhombic pellyite-like unit cell. The endotaxy, which was found for the first time and characterized by X-ray diffraction, is apparently not a rare phenomenon, but its observation by X-ray diffraction methods presents difficulties as well as high-resolution transmission electron microscopy is inapplicable because of the presence of hydrogen containing complexes of OH and H_2O in the compounds under study.

The presence of three endotaxic phases with the different ratios Eu:Si:O:H_2O = 1:6:15:2; 1 :6:17:2; and 1:4:12.5:5.5 (phases **I**, **II**, and **III**, respectively) in the same single crystal under study explains why attempts to determine the chemical formula of the compound by electron probe microanalysis failed.

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НОВИ (K-Eu) СИЛИКАТНИ ФАЗИ ОТ ГРУПАТА СЪЕДИНЕНИЯ С ОРТОРОМБИЧНА ЕЛЕМЕНТАРНА КЛЕТКА, ПОДОБНА НА ПЕЛИИТОВАТА

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(Резюме)

Чрез рентгенова дифракция са определени структурите на три синтетични фази на (K-Eu) силикати. Две от тези фази кристализират в нов структурен тип. Изчислени са техните кристалохимични формули и параметрите на елементарната им клетка, които са еднакви: a = 14.852(1) Å, b =15.902(1) Å, c = 7.243(1) Å, пр. гр. $P2_12_12$ (фаза I) и пр. гр. $Pbam$ (фази II и III). Структурите са решени с директни методи с използване на рентгенови дифракционни данни, получени от монокристал с фактори на достоверност R = 0.0271, 0.0479, и 0.0582, на базата съответно на 4370, 3320 и 2498 рефлекса ($|F| > 3\sigma(F)$). Кристалохимичните формули на фазите (Z=4) са $K_3Eu^{3+}[Si_6O_{15}]$. $2H_2O$, $K_3Eu^{3+}[Si_6O_{13}(OH)_4]$. $2H_2O$, и $K_3Eu^{3+}[Si_4O_{9.5}(OH)](OH)_2$. $5.5H_2O$. Структурата на фаза I се характеризира с силициево-кислородни слоеве $[Si_6O_{15}]$, аналогични на тези в изоструктурната фаза $K_3Nd[Si_6O_{15}] \cdot 2H_2O$. В структурите на фази II и III лентите $[Si_6O_{17}]$ и $[Si_8O_{21}]$ следват късата ос c и са свързани помежду си с Eu^{3+}-октаедри и тригонални призми, формирайки триизмерни слоисти и скелетни структури, включващи калиеви атоми между слоевете и в каналите.