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K_2GeF_6 COMPOUND CRYSTALLINE STRUCTURE ANALYSIS

Об'єктом дослідження є кристалічна структура поліморфної модифікації сполуки K_2GeF_6. Одним із проблемних місць є існування великої кількості дифракційних спектрів, отриманих з геометрією зйомки Брег-Бертрано в базі даних PDF-2 за 2004 рік. В даній роботі пропонується структурна модель для дифракційного спектру сполуки під номером 00-037-1154.

В ході дослідження використовувалася база даних PDF-2 за 2004 рік. А також програма HiphScorePlus 3.0, яка дозволяє уточнювати мікроструктурні параметри структурної моделі методом Рітвельда.

В результаті отримано, що даний дифракційний спектр досліджуваної сполуки може відповідати наступній структурній моделі:

– орторомбічна сингонія, просторова група симетрії Imma, періоди решітки a=8,3327 A°, b=5,891212 A°, c=5,908473 A°;
– мікроструктурні параметри Ge 16j x/a=0.172086, y/b=0.353968, z/c=0.291034;
– коефіцієнт заповнення позицій 0,25 K 16j x/a=0.316837, y/b=0.636701, z/c=0.134786;
– коефіцієнт заповнення позицій 0,5 F1 16j x/a=-0.087258, y/b=0.119218, z/c=0.783618;
– коефіцієнт заповнення позицій 0,5 F2 16j x/a=0.406830, y/b=-0.603655, z/c=0.376365;
– коефіцієнт заповнення позицій 0,5 F3 8f x/a=0.581125, y/b=0, z/c=0;
– коефіцієнт заповнення позицій 1,0;
– фактор розбіжності R=8,65453 %.

Аналізуючи отримані результати, можна припустити, що окрім двох відомих поліморфних модифікацій сполуки, а саме: тригональної та гексагональної сингоній, існує нова поліморфна модифікація і має власний структурний тип. Правильна система точок 16j для атомів германію, калію та фтору є не повністю заповненою.

Показано, що кристалічна структура сполуки зв'язана з її оптичними властивостями. Зокрема, кристали тригональної і гексагональної сингоній мають спектр поглинання в інфрачервоній області. Помічено також вплив кристалічної структури на спектри розсіяння цієї сполуки. Існує також розчеплення ліній випромінювання, що тісно пов'язане з будовою кристалічної ґратки. Тому вивчення даної поліморфної модифікації сполуки K_2GeF_6 дає можливість по новому розглядати та вивчати її оптичні властивості, завдяки яким вона може бути використана як люмінофор для комерційного виготовлення світлодіодів.

Ключові слова: *рентгеноструктурний аналіз, геометрія зйомки Брег-Бертрано, метод Рітвельда, кристалічна структура, сполука K_2GeF_6.*

1. Introduction

Potassium hexafluoro germanide K_2GeF_6 is formed by heating germanium dioxide with hydrofluoric acid and potassium fluoride, resulting in the precipitation of colorless poorly soluble crystals [1]. This salt does not decompose to a temperature of 500 °C and melts at 730 °C.

This compound is obtained using the chemical precipitation method, creating optimal preparation conditions for the red K_2GeF_6: Mn^{4+} phosphors. The obtained trigonal phase with the space group of symmetry P-3m1 of the K_2GeF_6:Mn^{4+} compound shows effective red emission, high-purity color, a fairly stable concentration of Mn^{4+} and low thermal hardening.

Polymorphic transformations at 400 °C are also observed into a hexagonal syngony with a spatial symmetry group of P63mc and at 500 °C in a cubic syngony with a spatial symmetry group of Fm3m. This compound of the hexagonal system has a peak of the zero red line with a wavelength of $\lambda=621$ nm. And at the same time in the cubic phase there are no emissions in the red region of the spectrum K_2GeF_6:Mn^{4+} crystals of trigonal and hexagonal systems can be promising materials for commercial red phosphors [2]. Therefore, studies of the crystal structure of this compound are relevant.

2. The object of research and its technological audit

The object of research is the crystal structure of the compound K_2GeF_6. The trigonal modification of K_2GeF_6 was synthesized by adding an aqualine MF solution to a solution of hydrofluorescent GeO_2 acid in a molar ratio of 1:1. The solution was evaporated in a water bath until a precipitate formed. Hexagonal modification of K_2GeF_6 was obtained by heating the trigonal modification for 18 hours at a temperature of 350 °C [3].

One of the most problematic places is the presence of a large number of diffraction spectra taken for a given compound, obtained by the Bragg-Bertrand method on copper filtered radiation. For example, in the PDF-2 database for 2004 [4], there are seven diffraction spectra of different quality, obtained for the compound K_2GeF_6, synthesized by various methods.

3. The aim and objectives of research

The aim of research is proposition of a structural model for the diffraction spectrum of the K_2GeF_6 compound number 00-037-11543 in the PDF-2 database by 2004.

To achieve this goal it is necessary to solve the following tasks:

1. To index the diffraction spectrum of the test compound and determine the lattice periods, syngonies, and space symmetry group.
2. To refine micro-parameters for the selected model using the Rietveld method.

4. Research of existing solutions of the problem

From the analysis of the literature it is known about two existing structural models of polymorphic modifications of the compound. Namely, from [5] it follows that the K_2GeF_6 compound has the structure of the beta-Rb_2GeF_6 SSG type (spatial symmetry group) P63mc (No. 186) with lattice periods a=5.7100 A°, b=5.7100 A°, c=9.2700 A°, α=90°, β=90°, γ=120°. The magnitude of the microstructural parameters is given in Table 1. The crystal structure is shown in Fig. 1.

Table 1

Microstructural parameters of the K_2GeF_6 compound according to [5]

Atom	Correct point system	Position fill ratio	x	y	z
Ge	2(b)	1	0.3333	0.6667	0.2500
K1	2(b)	1	0.3333	0.6667	0.8900
K2	2(a)	1	0.0000	0.0000	0.6100
F1	6(c)	1	0.1800	0.8200	0.3500
F2	6(c)	1	0.4900	0.5100	0.1500

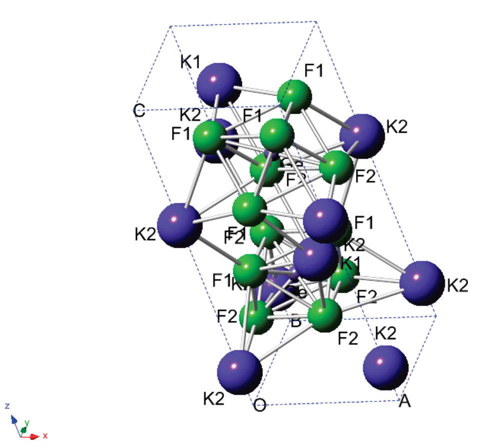

Fig. 1. K_2GeF_6 crystal structure (type beta-Rb_2GeF_6 SSG P63mc (No. 186))

According to [5], it follows that the K_2GeF_6 compound has a trigonal structure of a SSG P-3m1 (No. 164) with lattice periods a=5.6200 A°, b=5.6200 A°, c=4.6500 A°, α=90°, β=90°, γ=120°. The magnitude of the microstructural parameters is given in Table 2. The crystal structure is shown in Fig. 2.

Table 2

Microstructural parameters of the K_2GeF_6 compound according to [5]

Atom	Correct point system	Position fill ratio	x	y	z
K	2(d)	1	0.3333	0.6667	0.300
Ge	1(a)	1	0.0000	0.0000	0.0000
F	6(i)	1	0.8520	0.1480	0.2200

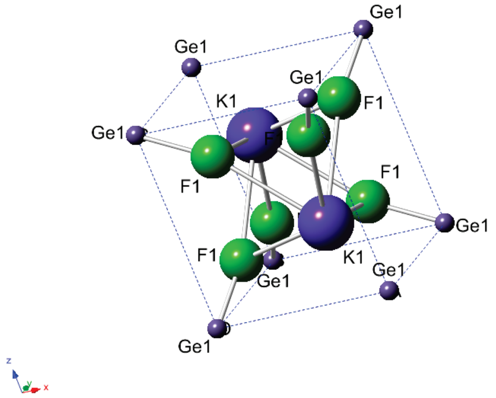

Fig. 2. K_2GeF_6 crystal structure (the trigonal structure of the SSG P-3m1 (No. 164))

In PDF-2 database for 2004 [4], there are seven diffraction spectra of this compound, obtained by X-ray powder diffraction (Bragg-Bertrand method) of different quality. Details of their crystal structure are given in Table 3.

Table 3

Information about the K_2GeF_6 crystal structure

№	Compound	Syngony, SSG	Lattice periods, A°	Card number in Pdf-2 database	Quality of the diffraction spectrum
1	K_2GeF_6	Trigonal P-3m1	a=5.632 b=5.632 c=4.668	00-007-0241	Highest quality of diffraction spectrum [6]
2	K_2GeF_6	Hexagonal	a=5.71 b=5.71 c=9.27	00-031-1021	Low spectrum accuracy [7]
3	K_2GeF_6	Cubic Fm-3m	a=8.357 b=8.357 c=8.357	00-037-1154	Pure phase [8]
4	K_2GeF_6	Cubic Fm-3m	a=8.1673 b=8.673 c=8.673	00-037-1155	Indexed [8]
5	K_2GeF_6	Hexagonal, P63mc	a=5.908 b=5.908 c=9.659	00-038-0854	Indexed [8]
6	K_2GeF_6	Trigonal P-3m1	a=5.62 b=5.62 c=4.65	01-073-1531	Calculated spectrum by structural model [5]
7	K_2GeF_6	Hexagonal, P63mc	a=5.71 b=5.71 c=9.27	01-075-0951	Calculated spectrum by structural model [4]

The diffraction spectrum of a high-quality K_2GeF_6 compound is given in [7] and corresponds to the trigonal crystal system, the structure model of which was proposed in [6].

The diffraction spectrum of the investigated K_2GeF_6 compound, which is indexed in hexagonal syngony, was proposed in [8]; however, the low quality of the spectrum raises doubts as to whether the given spectrum corresponds to the crystal structure of the compound. It should be noted that the proposed spectrum does not coincide with the model proposed in [5].

According to [9], the diffraction spectrum is 00-037-1155 in the PDF-2 database of the K_2GeF_6 compound obtained at 500 °C, at the number 00-038-0854 – at 440 °C, and 00-037-1154 – at 25 °C.

The last spectrum deserves special attention. According to [9], this diffraction spectrum is indexed in a cubic system and belongs to the space group Fm3m. In [2] it is noted that the transition to the cubic modification of the compound K_2GeF_6 occurs at a temperature of 500 °C.

The infrared absorption spectrum of trigonal and hexagonal K_2GeF_6 crystals was recorded in [3]. The hexagonal modification is characterized by a low integral intensity corresponding to the vibrations of octahedral $[GeF_6]^{-2}$ ions (about 20 %). This is due to an increase in the interaction and at the same time a decrease in the metal – fluorine interatomic distances. The existence of another structural modification is not specified.

The investigated compound of the trigonal system with the space group of symmetry P-3m1 is also observed by the authors of [10]. The octahedra are compressed along the trigonal axis. This leads to local symmetry, and affects the scattering spectra of this compound, which are caused by a Physics 165 laser, and were analyzed using a monochromator and a photodetector.

The optical properties of Mn^{4+} in some crystals, in particular in K_2GeF_6, which are closely related to the type of crystal lattice of the investigated materials, were investigated in [11, 12].

In particular, in [13], the method of simple synthesis of red phosphors by wet chemical etching of Ge in a mixed $HF/KMnO_4$ solution was used to obtain $K_2GeF_6{:}Mn^{4+}$. As a result, the trigonal syngony of the compound with the space group of symmetry P-3m1 was obtained. It has been observed that the splitting of radiation lines occurs due to the trigonal distortion of the crystal structure of the compound.

Thus, an analysis of the literature results indicates that the investigated compound can be used as red phosphors, the crystal structure of which affects its photoluminescent properties. In addition, two polymorphic transformations are observed, from trigonal to hexagonal and then cubic syngonies of the compound when it is heated.

5. Methods of research

The diffraction spectrum for the study was generated using the HiphScorePlus 3.0 program and the PDF-2 database attached to it for 2004. In the UDF format.

The analysis of the proposed structural model of this spectrum was also performed using the HiphScorePlus 3.0 program using the Rietveld method.

6. Research results

The diffraction spectrum of the compound is indexed in an orthorhombic system with lattice periods $a=5.929$ A°; $b=8.294$ A°; $c=5.914$ A°. Possible space group symmetry Imma (74).

The analysis of the proposed structural model of this spectrum was also performed using the HiphScorePlus 3.0 program using the Rietveld method.

The correct system of points and refined their coordinates for this spectrum are presented in Table 4.

Table 4

K_2GeF_6 microstructural parameters

Atom	Correct point system	x	y	z	Position fill ratio	U^a_{iso}
K1	16j	0.316837	0.636701	0.134786	0.500000	7.565899
Ge	16j	0.172086	0.353968	0.291034	0.250000	0.000000
F1	16j	–0.087285	0.119218	0.783618	0.500000	0.000000
F2	16j	0.406830	–0.603655	0.376365	0.500000	0.000000
F3	8f	0.581125	0.000000	0.000000	1.000000	6.566590

The magnitude of the interplanar distances and intensities, observed and calculated by this model, are given in Table 5.

Table 5

The magnitudes of interplanar distances and intensities, which are also observed and calculated

d_{cal}(A°)	d_{obs}(A°)	I_{cal}	I_{obs}	H	K	L
1	2	3	4	5	6	7
4.85001	4.85394	100.00	100.00	1	0	1
4.19431	4.18895	0.21	50.29	0	1	1
4.18880	–	52.30	–	2	0	0
2.96527	2.96398	77.69	89.86	0	0	2
2.95896	–	7.07	–	2	1	1
2.95657	–	6.18	–	0	2	0
2.52527	2.52099	9.96	59.83	1	1	2
2.52152	–	49.11	–	3	0	1
2.52123	–	9.76	–	1	2	1
2.41706	2.41399	24.69	49.98	2	0	2
2.41234	–	26.29	–	2	2	0
2.09115	2.08900	19.21	69.89	0	2	2
2.08841	–	52.74	–	4	0	0
1.92103	1.92100	3.53	5.13	1	0	3
1.91819	–	1.51	–	3	1	2
1.91641	–	2.35	–	3	2	1
1.87198	1.87399	4.52	5.14	0	1	3
1.86929	–	0.03	–	2	2	2
1.86782	–	3.48	–	4	1	1
1.86759	–	0.13	–	0	3	1
1.70776	1.70701	26.69	50.23	2	1	3
1.70580	–	6.40	–	4	0	2
1.70442	–	0.65	–	2	3	1
1.70414	–	0.55	–	4	2	0
1.60950	1.61001	24.51	50.22	3	0	3
1.60943	–	8.64	–	1	2	3
1.60768	–	3.57	–	1	3	2
1.60685	–	11.66	–	5	0	1
1.47949	1.47501	0.18	50.27	0	0	4
1.47635	–	1.05	–	4	2	2
1.47516	–	37.67	–	0	4	0
1.41417	1.41200	7.19	20.25	1	1	4
1.41256	–	1.71	–	3	2	3
1.41148	–	0.60	–	5	1	2
1.41138	–	0.25	–	3	3	2

Continuation of Table 5

1	2	3	4	5	6	7
1.41077	–	0.75	–	5	2	1
1.41062	–	2.59	–	1	4	1
1.39426	1.39000	0.02	5.11	2	0	4
1.39274	–	0.07	–	4	1	3
1.39265	–	0.58	–	0	3	3
1.39093	–	0.49	–	4	3	1
1.39082	–	0.52	–	6	0	0
1.39063	–	3.84	–	2	4	0
1.32219	1.32000	0.00	40.31	0	2	4
1.32085	–	5.33	–	2	3	3
1.31987	–	24.22	–	0	4	2
1.31947	–	12.82	–	6	1	1
1.27497	1.27400	8.30	30.31	3	1	4
1.27382	–	18.75	–	5	0	3
1.27236	–	3.19	–	3	4	1

The disagreement factor is $R=8.65453$ %. The refined lattice periods of the proposed structural model are $a=8.332702$ A°; $b=5.891212$ A°; $c=5.908473$ A°.

Table 6 shows the interatomic distances of the K_2GeF_6 compound number 00-037-1154 in the PDF-2 database by 2004.

Table 6

Interatomic distances of the investigated compound

Atom1	Atom2	Distance, A°	Atom1	Atom2	Distance, A°
1	2	3	4	5	6
K1	F1	1.193	F2	Ge	1.214
–	K1	1.335	–	F1	1.424
–	F3	1.416	–	F2	1.553
–	Ge	1.725	–	F2	1.724
–	K1	1.759	–	Ge	1.893
–	F1	1.865	–	F2	1.904
–	F1	1.975	–	F1	2.012
–	Ge	2.034	–	Ge	2.035
–	F2	2.146	–	F1	2.070
–	K1	2.208	–	K1	2.146
–	Ge	2.254	–	F3	2.308
–	K1	2.265	–	F2	2.320
–	F2	2.342	–	K1	2.342
–	Ge	2.402	–	K1	2.417
–	F2	2.417	–	Ge	2.434
–	F1	2.421	–	F2	2.457
–	F3	2.437	–	Ge	2.501
–	F1	2.441	–	F1	2.511
–	F3	2.476	–	F1	2.589
–	Ge	2.791	–	F3	2.725
–	F1	2.814	–	Ge	2.835
–	F2	2.854	–	K1	2.854
–	Ge	2.925	–	F3	2.876
–	F2	2.990	–	F1	2.906
–	F1	3.004	–	Ge	2.932
–	F3	3.027	–	K1	2.990
–	Ge	3.034	–	F1	2.994
–	K1	3.052	–	F2	3.010
–	F2	3.057	–	K1	3.057
–	Ge	3.070	–	F1	3.087
–	F2	3.118	–	F1	3.116
–	F3	3.173	–	K1	3.118
–	F2	3.189	–	Ge	3.139
–	F1	3.200	–	K1	3.189
–	Ge	3.265	–	F3	3.226
–	F2	3.323	–	F1	3.272
–	K1	3.332	–	F2	3.288
–	K1	3.349	–	F2	3.288
–	K1	3.349	–	K1	3.323
–	F2	3.353	–	K1	3.353
–	Ge	3.363	–	F1	3.433
–	F1	3.403	–	K1	3.467
–	Ge	3.425	–	F2	3.469
–	F2	3.467	F3	F3	1.352
Ge	F2	1.214	–	K1	1.416
–	Ge	1.225	–	K1	1.416
–	Ge	1.386	–	Ge	1.685
–	F3	1.685	–	Ge	1.685
–	K1	1.725	–	F1	1.818
–	F1	1.771	–	F1	1.818
–	Ge	1.850	–	F1	2.296
–	F2	1.893	–	F1	2.296
–	K1	2.034	–	F2	2.308
–	F2	2.035	–	F2	2.308
–	K1	2.254	–	K1	2.437
–	K1	2.402	–	K1	2.437
–	F2	2.434	–	K1	2.476
–	F2	2.501	–	K1	2.476
–	F3	2.539	–	Ge	2.539
–	F1	2.542	–	Ge	2.539
–	F3	2.592	–	Ge	2.592
–	F1	2.703	–	Ge	2.592
–	K1	2.791	–	F2	2.725
–	F3	2.815	–	F2	2.725
–	F2	2.835	–	F1	2.801
–	Ge	2.868	–	F1	2.801
–	F1	2.909	–	Ge	2.815
–	K1	2.925	–	Ge	2.815
–	F2	2.932	–	F2	2.876
–	F1	2.999	–	F2	2.876
–	Ge	3.010	–	F3	2.946
–	K1	3.034	–	F3	2.946
–	K1	3.070	–	K1	3.027
–	F1	3.084	–	K1	3.027
–	Ge	3.119	–	F1	3.124
–	F2	3.139	–	F1	3.124
–	F3	3.213	–	F1	3.132
–	F1	3.213	–	F1	3.132
–	F1	3.219	–	K1	3.173
–	K1	3.265	–	K1	3.173
–	F1	3.299	–	Ge	3.213
–	K1	3.363	–	Ge	3.213
–	F1	3.376	–	F2	3.226
–	F3	3.396	–	F2	3.226
–	K1	3.425	–	F3	3.241
–	F1	3.434	–	F3	3.241
–	F1	3.500	–	Ge	3.396
F1	K1	1.193	–	Ge	3.396
–	F2	1.424	–	–	–
–	F1	1.455	–	–	–
–	F1	1.541	–	–	–
–	Ge	1.771	–	–	–
–	F3	1.818	–	–	–
–	K1	1.865	–	–	–
–	K1	1.975	–	–	–

Continuation of Table 6

1	2	3	4	5	6
–	F2	2.012	–	–	–
–	F2	2.070	–	–	–
–	F1	2.119	–	–	–
–	F3	2.296	–	–	–
–	K1	2.421	–	–	–
–	K1	2.441	–	–	–
–	F2	2.511	–	–	–
–	Ge	2.542	–	–	–
–	F2	2.589	–	–	–
–	Ge	2.703	–	–	–
–	F1	2.741	–	–	–
–	F3	2.801	–	–	–
–	K1	2.814	–	–	–
–	F2	2.906	–	–	–
–	Ge	2.909	–	–	–
–	F1	2.917	–	–	–
–	F2	2.994	–	–	–
–	Ge	2.999	–	–	–
–	K1	3.004	–	–	–
–	Ge	3.084	–	–	–
–	F2	3.087	–	–	–
–	F2	3.116	–	–	–
–	F3	3.124	–	–	–
–	F3	3.132	–	–	–
–	F1	3.144	–	–	–
–	K1	3.200	–	–	–
–	Ge	3.213	–	–	–
–	Ge	3.219	–	–	–
–	F1	3.260	–	–	–
–	F2	3.272	–	–	–
–	Ge	3.299	–	–	–
–	Ge	3.376	–	–	–
–	K1	3.403	–	–	–
–	F2	3.433	–	–	–
–	Ge	3.434	–	–	–
–	Ge	3.500	–	–	–

Fig. 3 shows the resulting diffractograms, which are implanted and calculated by the proposed microstructural parameters of the K_2GeF_6 compound.

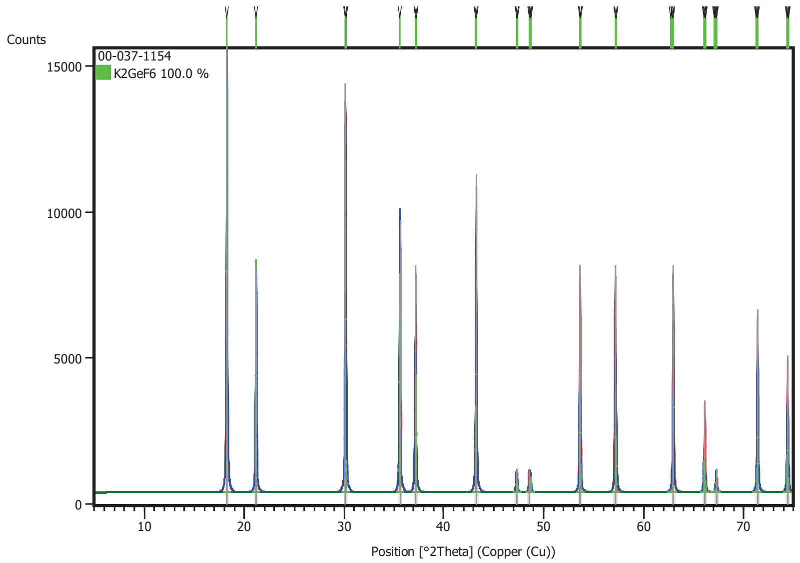

Fig. 3. The resulting diffraction of the K_2GeF_6 compound

Fig. 4 shows the K_2GeF_6 crystal structure of the orthorhombic syngony of the Imma space group, which belongs to its own type of structure.

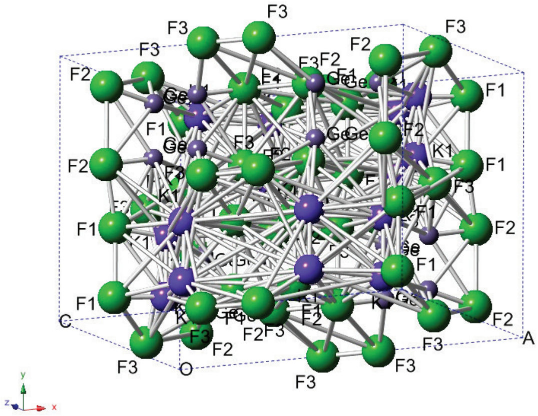

Fig. 4. Images of the crystal structure of the K_2GeF_6 compound

As can be seen from Fig. 4, fluorine and potassium atoms form irregular hexagons. In addition, these positions of atoms may not be completely filled, as for germanium atoms.

7. SWOT analysis of research results

Strengths. As a research result, the proposed structural model for the K_2GeF_6 diffraction spectrum numbered 00-037-1154 in the PDF-2 database for 2004. A check on the COD 2014 database did not reveal a similar structure. Therefore, it can be assumed that this structural model belongs to a new structural type.

Weaknesses. In the proposed structural model, the regular systems of 16*j* points have vacancies for germanium, potassium, and fluorine atoms (Table 4). Such situation can lead to a distortion of the crystal lattice of the investigated compound.

Opportunities. [2] indicated polymorphic transformation at 400 °C from trigonal to hexagonal and at 500 °C from hexagonal to cubic. However, it can be noted that the diffraction spectrum presented here does not refer to a cubic system, but has an orthorhombic system with vacancies in the correct system of points of 16*j*. These vacancies can occupy Mn atoms, the impurities of which are added to this compound to improve emission in LEDs [12].

Threats. The existing vacancies in the proposed structural model for the correct system of 16j points may also indicate a possible shift in the stoichiometric composition of the studied spectrum obtained for the K_2GeF_6 compound. Therefore, the crystal structure of this compound may require more detailed study. In particular, using the single crystal method or obtaining more reflexes with the Bragg-Bertrand geometry.

8. Conclusions

1. Conducted X-ray phase analysis did not reveal the presence of several phases

in the tested compound, presented in Table 1. So it is possible to conclude that the connection is single phase.

Using the TREOR program for indexing radiographs of the K_2GeF_6 compound number 00-037-1154 in the PDF-2 database for 2004.

The diffraction spectrum of the compound is indexed in an orthorhombic system with lattice periods a=8.3327 A°, b=5.891212 A°, c=5.908473 A°. Possible space group symmetry Imma (74).

2. Using the HiphScorePlus 3.0 program, the diffraction spectrum of the compound numbered 00-037-1154 was investigated using the Rietveld method. A structural model is proposed: the spatial symmetry group Imma (74). The refined lattice periods of the proposed structural model are a=8.3327 A°, b=5.891212 A°, c=5.908473 A°. The disagreement factor is R=8.65453 %. Microstructural parameters are given in Table 4.

The crystal structure of this compound may belong to a new type of structure.

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