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# КОМП'ЮТЕРНІ НАУКИ ТА ІНФОРМАЦІЙНІ ТЕХНОЛОГІЇ

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## COMPUTER SCIENCE AND INFORMATION TECHNOLOGY

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### CRYSTAL STRUCTURE OF $K_3TiOF_5$ COMPOUND

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**Zavodyannyi V.V.** – Candidate of Physical and Mathematical Sciences,  
Associate Professor at the Department of Hydraulic Engineering  
Kherson State Agrarian and Economic University  
ORCID ID: 0000-0002-8224-8215

The object of research is the crystal structure of the  $K_3TiOF_5$  compound. It is known from the literature that this material is ferroelectric. The dielectric constant of materials is very high. Therefore, this material can be used in capacitors, which are much smaller in dielectric size. Relatively recently, a number of materials with ferroelectric properties have been synthesized, including  $K_3TiOF_5$ . The diffraction spectrum of the compound was taken by the powder method with the Bragg-Bertrand shooting geometry and is presented in the PDF-2 database for 2009 under the number 00-023-0506 indexed in the tetragonal system, with lattice periods  $a=6,102^\circ A$ ,  $c=8,655^\circ A$ . To date, there is no complete information on the crystal structure of this compound.

The study used a 2009 PDF-2 database. And also, the HighScorePlus 3.0 program (Netherlands), which allows to refine the microstructural parameters of the structural model by the Rietveld method.

The diffraction spectrum for the study was generated using the HighScorePlus 3.0 program and the attached pdf-2 database for 2009 in UDF format.

As a result, it was found that the given diffraction spectrum of the compound under study can correspond to the following structural model: the diffraction spectrum of the  $K_3TiOF_5$  compound is indexed in the tetragonal system with lattice periods  $a = 6.086^\circ A$ ;  $b = 6.086^\circ A$ ;  $c = 8.675^\circ A$ . The space group of symmetry  $I41 (80)$  is possible:

- microstructural parameters  $K1\ 8b\ x/a = 0.252\ (9)$ ,  $y/b = 0.588\ (4)$ ,  $z/c = 0.2\ (4)$ ;
- position filling factor  $0.5\ K2\ 8b\ x/a = 0.233\ (5)$ ,  $y/b = 0.233\ (5)$ ,  $z/c = 0.4\ (4)$ ;
- position filling factor  $1.0\ F1\ 8b\ x/a = -0.900\ (8)$ ,  $y/b = 0.393\ (4)$ ,  $z/c = 0.1\ (4)$ ;
- position filling factor  $1.0\ F2\ 8b\ x/a = 0.749\ (7)$ ,  $y/b = 0.262\ (7)$ ,  $z/c = 0.8\ (4)$ ;
- position filling factor  $1.0\ F3\ 8b\ x/a = 0.47\ (1)$ ,  $y/b = 0.696\ (9)$ ,  $z/c = -0.1\ (4)$ ;
- position filling factor  $0.5$ ;  $Ti1\ 8b\ x/a = 0.247\ (5)$ ,  $y/b = 0.803\ (4)$ ,  $z/c = 0.1\ (4)$ ;
- position filling factor  $0.5$ ;  $O1\ 8a\ x/a = 0.0$ ,  $y/b = 0.0$ ,  $z/c = 0.1\ (4)$ ;
- position filling factor  $1.0$ ;
- disagreement factor  $R = 7.311\%$ .

Analyzing the results obtained, it can be assumed that the studied structure of the compound crystallizes in its own structural type.

The study of the crystal structure of a compound contributes to a better understanding of its physical properties, in particular, ferroelectric.

**Key words:** X-ray structural analysis, Bragg-Bertrand survey geometry, Rietveld method, crystal structure,  $K_3TiOF_5$  composition.

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### **Заводяний В.В. Кристалічна структура сполуки $K_3TiOF_5$**

Об'єктом дослідження є кристалічна структура сполуки  $K_3TiOF_5$ . З літературних даних відомо, що цей матеріал – сегнетоелектрик. Діелектрична проникність матеріалів дуже велика. Тому такий матеріал може бути використаний у конденсаторах, які значно менші за розмірами за діелектричні. Порівняно недавно було синтезовано низку матеріалів, що мають сегнетоелектричні властивості, до яких належить і  $K_3TiOF_5$ . Дифракційний спектр сполуки, що знятий по методу порошку з геометрією зйомки Брег-Бертрано, представлений у базі даних PDF-2 за 2009 рік під номером 00-023-0506, індексується в тетрагональній сингонії з періодами решітки  $a=6,102^\circ\text{Å}$ ,  $c=8,655^\circ\text{Å}$ . Повні відомості про кристалічну структуру такої сполуки на тепер відсутні.

У ході дослідження використовувалася база даних PDF-2 за 2009 рік. А також програма HighScorePlus 3.0 (Нідерланди), яка дозволяє уточнювати мікроструктурні параметри структурної моделі методом Ритвельда.

Дифракційний спектр для дослідження генерували за допомогою програми HighScorePlus 3.0 та приєднаної до неї бази даних PDF-2 за 2009 р. у форматі UDF.

У результаті отримано, що цей дифракційний спектр досліджуваної сполуки може відповідати такій структурній моделі: дифракційний спектр сполуки  $K_3TiOF_5$  індексується в тетрагональній сингонії з періодами решітки  $a=6.086\text{ Å}$ ;  $b=6.086\text{ Å}$ ;  $c=8.675\text{ Å}$ . Можлива просторова група симетрії I41 (80):

- мікроструктурні параметри  $K1\ 8b\ x/a=0.252(9)$ ,  $y/b=0.588(4)$ ,  $z/c=0.2(4)$ ;
- коефіцієнт заповнення позицій  $0.5\ K2\ 8b\ x/a=0.233(5)$ ,  $y/b=0.233(5)$ ,  $z/c=0.4(4)$ ;
- коефіцієнт заповнення позицій  $1,0\ F1\ 8b\ x/a=-0.900(8)$ ,  $y/b=0.393(4)$ ,  $z/c=0.1(4)$ ;
- коефіцієнт заповнення позицій  $1,0\ F2\ 8b\ x/a=0.749(7)$ ,  $y/b=0.262(7)$ ,  $z/c=0.8(4)$ ;
- коефіцієнт заповнення позицій  $1,0\ F3\ 8b\ x/a=0.47(1)$ ,  $y/b=0.696(9)$ ,  $z/c=-0.1(4)$ ;
- коефіцієнт заповнення позицій  $0,5$ ;  $Ti1\ 8b\ x/a=0.247(5)$ ,  $y/b=0.803(4)$ ,  $z/c=0.1(4)$ ;
- коефіцієнт заповнення позицій  $0,5$ ;  $O1\ 8a\ x/a=0.0$ ,  $y/b=0.0$ ,  $z/c=0.1(4)$ ;
- коефіцієнт заповнення позицій  $1,0$ ;
- фактор розбіжності  $R=7,311\%$ .

Аналізуючи отримані результати, можна припустити, що досліджувана структура з'єднання кристалізується у власному структурному типі.

Вивчення кристалічної структури сполуки сприяє кращому розумінню його фізичних властивостей, зокрема сегнетоелектричних.

**Ключові слова:** рентгеноструктурний аналіз, геометрія зйомки Брег-Бертран, метод Ритвельда, кристалічна структура, склад  $K_3TiOF_5$ .

### **Introduction**

Ferroelectric materials are used in variable capacitors. The dielectric constant of ferroelectric materials is not only tunable but also very high. Therefore, ferroelectric capacitors are much smaller in size and have a higher electrical capacity than dielectric capacitors. In comparison, a number of materials with ferroelectric properties have recently been synthesized, including  $K_3TiOF_5$  [1]. Starting materials KF (Ventron, purity > 99.9%), oxides  $TiO_2$ ,  $Nb_2O_5$ ,  $Ta_2O_5$ ,  $WO_3$  (Cerac, 99,95%) pre-dried in vacuum at 473K for 20 hours. Oxyfluorides  $TiOF_2$ ,  $NbO_2F$ ,  $TaO_2F$  are obtained by the action of a 40% solution of hydrofluoric acid on the corresponding oxides in a Teflon bath, after complete evaporation of the solution in a sand bath at 373K. Residual solids are degassed in vacuum at a temperature of 473K. About 18 g of the mixture is weighed in stoichiometric proportions, ground in an agate mortar in an oven, then placed in a Biconical platinum 10% rhodium crucible. The compound is obtained in the following reaction  $3KF+TiOF_2 \rightarrow K_3TiOF_5$ . After degassing in vacuum for 20 hours at 473K and then sealing in a dry oxygen atmosphere, the crucible is fired at a reaction temperature for 24 hours and then at a melting temperature of + 50K [1].

**The object of research** is the crystal structure of the  $K_3TiOF_5$  compound.

PDF-2 database for 2009 contains indexed diffraction spectrum obtained for the  $K_3TiOF_5$  compound. The crystal structure of this spectrum is unknown.

### **The aim and objectives of research**

*The aim of research* is to propose a structural model for the diffraction spectrum of the  $K_3TiOF_5$  compound under the number 00-023-0506 in the PDF-2 database for 2009.

To achieve this aim, it is necessary to solve the following objectives:

1. Determine the periods of the lattice and the crystal system in which the studied compound crystallizes.
2. Select the space group of symmetry and propose a structural model for the given spectrum of the compound.
3. Carry out the refinement of microstructural parameters for the selected model by the Rietveld method.

Solvothermal synthesis of  $K_3TiOF_5$  was carried out in a stainless steel autoclave with a Teflon lining at reduced pressure. All reagents ( $KOH$ ,  $KF \cdot 2H_2O$ ,  $TiO_2$ ,  $Ti$ ,  $NH_4HF_2$ ,  $H_2O_2$ ) and methanol were analytically pure and used without further purification (purchased by Shanghai Chemical Reagent Company). The mixture is placed in a stoichiometric ratio in a teflon-lined stainless steel autoclave of milliliters, which is then filled with methanol to 80 times the total volume. The autoclave was quickly closed and heated at  $200^\circ C$  for 24 or 36 hours and cooled naturally to room temperature. The precipitates were collected and washed with ethanol, distilled water, and dried in a vacuum at  $60^\circ C$  for 2 hours [3].

Diffraction patterns were taken from the obtained sample by the powder method with the Bragg-Bertrand geometry. The diffraction spectrum corresponds to  $K_3TiOF_5$  numbered 00-023-0506 in the PDF-2 database [2; 3], indexed in the tetragonal system, with lattice periods  $a=6,102^\circ A$ ,  $c=8,655^\circ A$ .

The results of the analysis of the literature indicate that the crystal structure of the test compound is unknown. With its electrical properties it can be used as a ferroelectric.

#### Methods of research

The diffraction spectra of the compounds for the study were generated using HighScorePlus 3.0 and the attached PDF-2 database for 2009 in UDF format.

Analysis of the proposed structural model of this spectrum was performed using the program HighScorePlus 3.0 by the Rietveld method.

#### Research results

The diffraction spectrum of the compound  $K_3TiOF_5$  is indexed in tetragonal synony with lattice periods  $a=6.086 A^\circ$ ;  $b=6.086 A^\circ$ ;  $c=8.675 A$ . Possible symmetry group I41 (80).

The correct system of points and their specified coordinates for this spectrum are presented in Table 1.

Table 1  
Microstructural parameters of  $K_3TiOF_5$  for spectrum 00-023-0506  
in PDF-2 database up to 2009

Atom	Wyck.	s.o.f.	x	y	z	$U_{iso}^a$
K1	8b	0.500000	0.252(9)	0.588(4)	0.2(4)	0(1)
K2	8b	1.000000	0.233(5)	0.233(5)	0.4(4)	5.8(4)
F1	8b	1.000000	-0.900(8)	0.393(4)	0.1(4)	10(1)
O1	4a	1.000000	0.000000	0.000000	0.1(4)	0(1)
F2	8b	1.000000	0.749(7)	0.262(7)	0.8(4)	0(1)
F3	8b	0.500000	0.47(1)	0.696(9)	-0.1(4)	0(2)
Ti1	8b	0.500000	0.247(5)	0.803(4)	0.1(4)	0(1)

Note: Wyck. – correct point system; s.o.f. – position filling factor with atoms; x, y, z – coordinates of atoms in the fate of lattice periods ( $x=X/a$ ;  $y=Y/b$ ;  $z=Z/c$ );  $U_{iso}$  – temperature factor

The values of observed and calculated interplanar distances and integral intensities of the diffraction spectra are given in Table 2.

Table 2

The values of interplanar distances and intensities are given in [2],  
and calculated according to this model

$d_{cal}$ ( $\text{\AA}^{\circ}$ )	$d_{obs}$ ( $\text{\AA}^{\circ}$ )	$I_{cal}$	$I_{obs}$	H	K	L
1	2	3	4	5	6	7
4.94655	4.94993	13.62	10.18	0	1	1
	4.31978		5.07			
4.27702	4.27999	6.24	5.11	1	1	0
3.04189		1.25		1	1	2
3.03006	3.02998	100.00	100.00	0	2	0
2.60241		0.75		0	1	3
2.58765		0.58		1	2	1
2.58765		1.10		2	1	1
2.48259	2.48098	14.95	20.18	0	2	2
2.16240	2.16201	14.37	15.10	0	0	4
2.14553	2.14599	26.43	30.39	2	2	0
1.97672	1.93400	0.30	5.12	1	2	3
1.97672		1.74		2	1	3
1.97024		1.13		0	3	1
1.93177		5.98		1	1	4
1.92271		0.89		2	2	2
1.91972		0.10		1	3	0
1.91972		0.89		3	1	0
1.76209		4.91		0	2	4
1.75521	1.75600	1.48	15.23	3	1	2
1.75521		8.14		0	1	5
1.66499	1.66301	1.08	5.06	0	3	3
1.65726	1.65299	0.62	5.15	2	3	1
1.65343		4.07		3	2	1
1.65343		0.63		2	2	4
1.52462	1.52501	8.86	15.18	0	4	0
1.51868	1.51800	8.66	10.14	1	2	5
1.46044		0.06		2	1	5
1.46044		0.33		2	3	3
1.45522	1.45400	0.50	5.10	3	2	3
1.45522		0.44		1	4	1
1.45263		0.87		4	1	1
1.45263		0.50		1	3	4
1.43702	1.43200	0.59	5.11	3	1	4
1.43702		0.53		0	4	2
1.43328		1.94		3	3	0

Table 2 (Continued)

1	2	3	4	5	6	7
1.43204		0.43		1	1	6
1.36835	1.36900	0.16	5.04	3	3	2
1.35979	1.35900	0.34	10.21	2	4	0
1.35873		1.15		4	2	0
1.35873		1.68		0	3	5
1.31656		0.23		1	4	3
1.31273		0.20		4	1	3
1.31273		1.35		0	2	6
1.30398		1.04		2	4	2
1.29657		0.09		4	2	2
1.29657		0.07		0	1	1

Disagreement factor  $R = 7.311\%$ .

Table 3 shows the interatomic distances of the proposed structural model for the  $K_3TiOF_5$  compound for spectrum 00-023-0506 in the PDF-2 database for 2009.

Table 3

#### Interatomic distances of the $3TiOF_5$ compound

Atom <sup>1</sup>	Atom <sup>2</sup>	Distance, Å <sup>o</sup>
1	2	3
K1	- Ti1	1.343
	- F2	1.421
	- F1	1.558
	- F2	1.576
	- Ti1	2.130
	- F1	2.177
	- K2	2.235
	- F1	2.278
	- O1	2.300
	- F3	2.360
	- F3	2.479
	- K1	2.578
	- K2	2.661
	- Ti1	2.684
	- F1	2.800
	- O1	2.988
	- F3	3.018
	- F3	3.126
	- K1	3.206
	- K2	3.208
	- K1	3.246
	- F2	3.267
	- K2	3.357
	- K2	3.389

Table 3 (Continued)

1	2	3
K2	- F1	1.394
	- F3	1.787
	- O1	2.133
	- K2	2.176
	- F3	2.195
	- K1	2.235
	- F1	2.344
	- Ti1	2.634
	- K1	2.661
	- F1	2.682
	- O1	2.946
	- F2	2.973
	- F2	3.003
	- Ti1	3.011
	- F3	3.021
	- Ti1	3.116
	- O1	3.166
	- F1	3.170
	- K1	3.208
	- F2	3.219
	- F2	3.248
	- Ti1	3.260
	- F2	3.348
	- K1	3.357
	- K1	3.389
	- F3	3.399
	- F3	3.430
	- F2	3.458
	- Ti1	3.480
	- Ti1	3.494
F1	- K2	1.394
	- K1	1.558
	- F1	1.783
	- K1	2.177
	- O1	2.211
	- K1	2.278
	- K2	2.344
	- Ti1	2.425
	- O1	2.469
	- F2	2.509
	- F2	2.536

Table 3 (Continued)

1	2	3
	- Ti1	2.656
	- F2	2.679
	- K2	2.682
	- F2	2.771
	- K1	2.800
	- F1	2.808
	- F3	2.910
	- Ti1	3.016
	- F3	3.098
	- F3	3.106
	- K2	3.170
	- Ti1	3.182
	- Ti1	3.264
	- F3	3.324
	- Ti1	3.331
	- F3	3.355
O1	- Ti1	1.939
	- F3	1.994
	- K2	2.133
	- F1	2.211
	- K1	2.300
	- F2	2.302
	- F1	2.469
	- F2	2.569
	- K2	2.946
	- K1	2.988
	- Ti1	3.065
	- Ti1	3.098
	- F3	3.137
	- K2	3.166
F2	- Ti1	0.976
	- Ti1	1.274
	- K1	1.421
	- F3	1.519
	- K1	1.576
	- F3	1.958
	- F2	2.171
	- O1	2.302
	- F1	2.509
	- F1	2.536

Table 3 (Continued)

1	2	3
	- O1	2.569
	- F1	2.679
	- F1	2.771
	- K2	2.973
	- K2	3.003
	- Ti1	3.114
	- K2	3.219
	- K2	3.248
	- F3	3.252
	- K2	3.253
	- F3	3.263
	- K1	3.267
	- K2	3.348
	- Ti1	3.434
	- F3	3.438
	- K2	3.458
F3	- Ti1	1.184
	- F2	1.519
	- K2	1.787
	- F2	1.958
	- O1	1.994
	- K2	2.195
	- Ti1	2.259
	- K1	2.360
	- F3	2.415
	- K1	2.479
	- F1	2.910
	- F3	2.921
	- Ti1	2.970
	- K1	3.018
	- K2	3.021
	- F1	3.098
	- Ti1	3.099
	- F1	3.106
	- K1	3.126
	- O1	3.137
	- F2	3.252
	- F2	3.263
	- F3	3.269
	- F1	3.324
	- F1	3.355



Table 3 (Continued)

1	2	3
	- K2	3.399
	- K2	3.430
	- F2	3.438
Ti1	- F2	0.976
	- F3	1.184
	- F2	1.274
	- K1	1.343
	- O1	1.939
	- K1	2.130
	- Ti1	2.216
	- F3	2.259
	- F1	2.425
	- K2	2.634
	- F1	2.656
	- K1	2.684
	- F3	2.970
	- K2	3.011
	- F1	3.016
	- O1	3.065
	- O1	3.098
	- F3	3.099
	- F2	3.114
	- K2	3.116
	- F1	3.182
	- K2	3.260
	- F1	3.264
	- F1	3.331
	- F2	3.434
	- K2	3.480
	- K2	3.494

Fig. 1 shows diffraction patterns generated and calculated from the structural simulator for the  $K_3TiOF$  compound.

Fig. 2 shows an image of the proposed model of the crystal structure of the investigated compound.

The space group of symmetry  $I4_1$  (80) has a rotary axis of symmetry of the 2nd order parallel to 001, a helical axis of the 4th order with translation  $1/3 c$  parallel to 001.

Also, partial filling of the correct systems of points in the structure under study may indicate that the stoichiometric composition of the compound may be slightly changed. So, the structure of the connection requires further investigation.

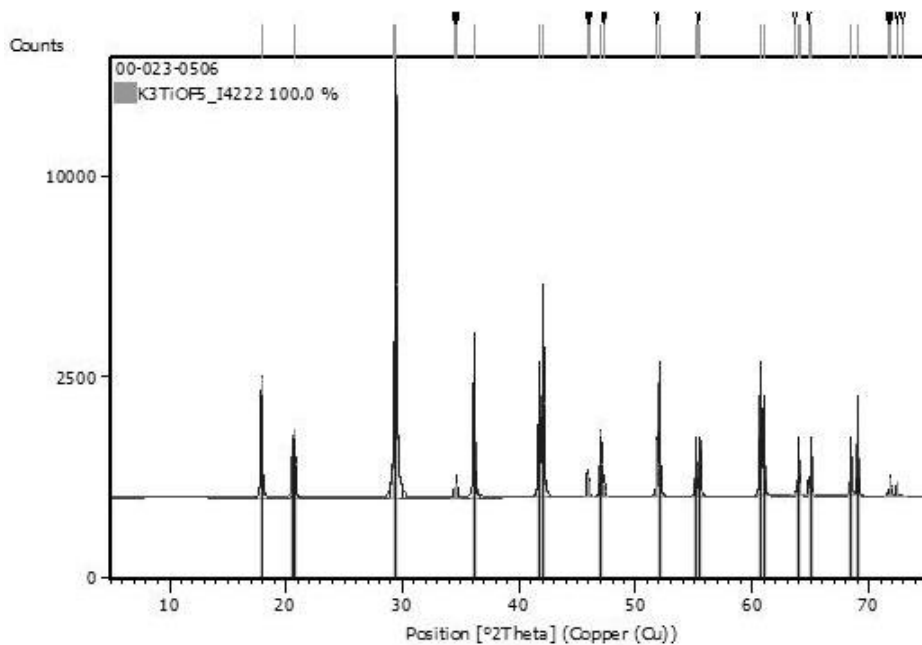


Fig. 1. The resulting X-ray diffraction pattern of the  $K_3TiOF_5$  compound generated and calculated from the structural modeling

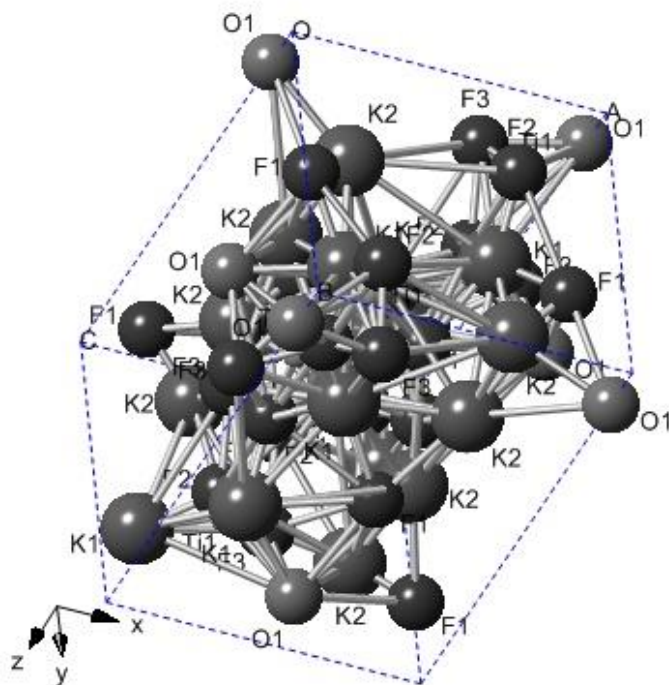


Fig. 2. Crystal structure of the  $K_3TiOF_5$  compound for the investigated diffraction spectrum

### Conclusions

1. Using the TREOR program, the diffraction spectrum of the  $K_3TiOF_5$  compound is indexed in the tetragonal system with lattice periods  $a=6.086 \text{ \AA}$ ;  $b=6.086 \text{ \AA}$ ;  $c=8.675 \text{ \AA}$ .

The diffraction spectrum of the  $\beta$ -phase (compound 00-049-0903) is indexed in the orthorhombic system with lattice periods  $a=8.668(7) \text{ \AA}$ ;  $b=8.677(8) \text{ \AA}$ ;  $c=8.685(7) \text{ \AA}$ .

2. The space group of symmetry  $I41 (80)$  is possible and proposed for the calculation of the structural model.

3. Using the HighScorePlus 3.0 software, the parameters of the structural model of the compound under study were refined by the Rietveld method. Microstructural parameters are given in Table 1.

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