of the given crystallographic problem by the program for orientational electron microdiffraction analysis of two-phase structures.

In conclusion the authors thank A. F. Rebeko and S. N. Kabuzenko for help in adapting the OMEGA program to the ES-1020 computer.

[1)] As usual, reciprocal space is denoted by an asterisk.

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Use of modern x-ray equipment to solve fine problems of structural mineralogy by the example of the crystal structure of babefphite $BaBe(PO_4)F$

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Using a $P\bar{1}$ automatic diffractometer the authors have determined the true triclinic symmetry of babefphite $BaBe(PO_4)F$ (FL); from this viewpoint they have refined the positions of the Be, P, O, and F atoms occupying independent crystallographic positions ($R_{hkl} = 4.1\%$).

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In 1967 we were involved in the first determination of the crystal structure of babefphite $Ba(Be, P)_2O_4F$ (Ref. 1) on the basis of photographic material for projections yz (60 reflections, $R_{0kl} = 7.6\%$) and xy (70 reflections, $R_{hk0} = 8.7\%$), with 86 reflections with hkl scanning for their correlation.

In the structure of babefphite, solved in the space group Fdd2 ($a = 6.93$; $b = 16.74$; $c = 6.93$ Å; $d = 4.31$ g/cm^3; $z = 8$) with 16 general positions and 8 special positions on the dyad rotation axes, eight Be atoms and eight P atoms statistically filled the general 16-fold position. But in this Fdd2 space group it was also necessary to postulate statistical filling of one of the 16-fold positions jointly by eight O atoms and eight F atoms. The second type of anions, O_2 atoms, entirely filled the 16-fold position, whereas the O_1 atoms occupied special 8-fold positions on the $L_2(00z)$ axes. Nevertheless, even in Ref. 1 it was noted that probably the free ("dangling") vertices of the P-tetrahedra are occupied by O^{2-} ions, whereas in the Be tetrahedra they are occupied by F^{1-} ions, provided that the Be and P atoms can be ordered in the context of a space group with lower symmetry; this was previously shown in a number of interpreted Be phosphate structures – herderite, hurlbatite, and beryllonite, in which Be and P occupy different but "qualitatively" very similar positions.[2]

The appearance and adoption of the Syntex $P\bar{1}$ precision automatic four-circle diffractometer and of E-XTL specialized systems for determining crystal structures enabled us to attack the problem of the appearance of ordering of Be (Z = 4) and P (Z = 15), O (Z = 8) and Fe (Z = 9) against the background of very heavy (Z = 59) Ba atoms.

For this investigation we selected an isometric crystal giving reflections of satisfactory quality on the Laue diffraction patterns and measuring 0.12 × 0.15 × 0.17 mm; it was obtained from the A. E. Fersman Mineralogical Museum, Academy of Sciences of the USSR (specimen No. 72,021). The subsequent investigations were performed on a $P\bar{1}$ automatic diffractometer, enabling us to obtain, in particular, x-ray oscillation photographs about any selected direction from the unoriented single crystal. An analysis of the list of possible lattice vectors indicated by the autoindexing program pointed to the presence of three mutually perpendicular directions with identity periods similar to those given in Ref. 1. To ascertain the Laue symmetry we took around these directions x-ray oscillation photographs on polaroid film (oscillation interval 20°, exposure of each x-ray photograph 1 h 20 min). Weak reflections disturbing the symmetry line were revealed on two of these photographs, corresponding to the b and c periods; reflections clearly disturbing the symmetry line were not observed on the third x-ray oscillation photograph along the *a* axis. However, taking these axes as basal, and refining the parameters *a*, b, c, α, β, γ, we obtained: $a = 6.889(3)$; $b = 16{,}814(7)$; $c = 6.902(3)$ Å; $\alpha = 90.01\ (3)$; $\beta = 89.99\ (3)$; $\gamma = 90.32\ (3)°$.[1)] An analysis of the symmetry of the x-ray oscillation photographs and of our values for the angles α, β, and γ indicated triclinic symmetry of the mineral and compelled us to record a three-dimensional set of

TABLE I. Balance of Valence Forces on Anions According to Pauling in the Structure of Babefphite BaBe[PO_4]F

Atom	Ba_1	Ba_2	Be_1	Be_2	P_1	P_2	Σ+
O_1	2/9×2	2/9	–	–	5/4	–	1 11/12
O_2	2/9	–	–	1/2	5/4	–	1 35/36
O_3	–	2/9	1/2	–	–	5/4	1 35/36
O_4	–	2/9	–	1/2	–	5/4	1 35/36
O_5	2/9	2/9×2	–	–	–	5/4	1 11/12
O_6	–	2/9	1/2	–	5/4	–	1 35/36
O_7	2/9	–	1/2	–	5/4	–	1 35/36
O_8	2/9	–	–	1/2	–	5/4	1 35/36
F_1	2/9	2/9×2	1/2	–	–	–	1 1/6
F_2	2/9×2	2/9	–	1/2	–	–	1 1/6

TABLE II. Coordinates of Basis Atoms and Isotropic and Anisotropic Temperature Corrections in the Structure of Babefphite BaBe[PO_4]F

Atom	x/a	y/b	z/c	B_{iso}
Ba_1	0	0	0	0,78(1)
Ba_2	0,250	0.250	0,250	0.68(0)
Be_1	0,264(2)	0.1703(7)	0,741(2)	0,5(1)
Be_2	0.514(2)	0.4184(6)	0.511(1)	0,4(1)
P_1	0,0099(3)	0,0828(1)	0.4895(3)	0,38(2)
P_2	0.2603(3)	0.3325(1)	0,7609(3)	0.32(2)
O_1	0,1637(9)	0.0794(4)	0,3334(9)	0,82(8)
O_2	0.8981(8)	0,0026(3)	0,5002(9)	0,73(8)
O_3	0,1467(8)	0,2521(4)	0,7498(9)	0.74(8)
O_4	0,3499(9)	0.3488(4)	0,5601(8)	0.75(8)
O_5	0,4127(9)	0.3291(4)	0,9167(9)	0,82(8)
O_6	0,3599(9)	0,1483(4)	0,9479(8)	0,72(8)
O_7	0.1002(9)	0,0981(4)	0.6904(8)	0,64(7)
O_8	0,1086(9)	0,3991(4)	0,8014(9)	0.70(7)
F_1	0,4180(8)	0,1741(4)	0,5818(8)	0.90(7)
F_2	0,1682(8)	0,4235(3)	0.1685(8)	0.84(7)

$$T = \exp\left[-1/4\left(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*\right)\right]$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba_1	0,58(1)	0,95(1)	0.83(1)	−0,15(1)	0,03(1)	0,07(1)
Ba_2	0,67(1)	0.77(1)	0.72(1)	−0,03(1)	0.04(1)	−0,13(1)
Be_1	1.0(3)	0.8(3)	1,0(3)	−0,6(3)	0.5(3)	0,4(3)
Be_2	1,0(3)	0,5(3)	0,3(2)	−0,0(2)	−0,6(2)	0,1(2)
P_1	0.31(5)	0.40(5)	0,42(5)	−0.15(4)	−0,00(4)	0,01(4)
P_2	0,36(5)	0,30(5)	0.38(5)	−0,01(4)	0,02(4)	−0,01(4)
O_1	0,8(2)	1.0(2)	0.8(2)	0.0(1)	0,3(1)	−0,1(1)
O_2	0.6(2)	0.4(1)	1.3(2)	−0,1(1)	0,1(1)	−0,2(1)
O_3	0,5(1)	0,4(1)	1,5(2)	0.01	0.0(1)	0,1(1)
O_4	1.0(2)	0,8(2)	1,6(1)	−0,5(1)	0,3(1)	−0,2(1)
O_5	0.7(2)	1.0(2)	0,8(2)	0,0(1)	−0.2(1)	−0,1(1)
O_6	0,9(2)	0.7(2)	0.7(2)	0,0(1)	−0,2(1)	−0,0(1)
O_7	0,8(2)	0.7(2)	0.6(1)	−0,2(1)	−0,2(1)	0,0(1)
O_8	1.0(2)	0.7(2)	0.7(2)	0,1(1)	0,2(1)	−0,0(1)
F_1	0,8(2)	1,2(2)	0.9(2)	−0,2(1)	0,2(1)	0,0(1)
F_2	0.7(1)	1,0(2)	0,9(2)	−0,2(1)	−0.1(1)	−0,1(1)

4102 independent nonzero ($I \geq 1.96\ \sigma I$) reflections ($2\theta:\theta$ method, variable scanning rate 6–24 deg/min, Mo $K\alpha$ radiation, max $\sin\theta/\lambda$ = 1.08 Å^{-1}) for babefphite as for a triclinic crystal, permitting an investigation of the structure in the context of any symmetry group.

An analysis of the resulting diffractometric set of intensities confirmed the F cell of the mineral structure and revealed a whole series of weak reflections contradicting the diamond planes d, i.e., the Fdd2 group. If we keep within the orthorhombic symmetry, the only possible space group is Fmm2. An analysis of the Patterson function showed that it was impossible to distribute the basis atoms within this Fedorov group. In going over to the space group F112, i.e., with a decrease in the symmetry to monoclinic, the general 16-fold positions of the Fdd2 group are subdivided into two 8-fold positions; this undoubtedly enables us to separate the P and Be and the O and F atoms while retaining the Ba atoms in the special 4-fold positions, making the reservation that instead of one Ba basis atom with multiplicity 8 we have 2Ba in 4-fold positions on the L_2 axes linked with the pseudoplane d. Calculation of the three-dimensional electron density distribution permitted location of the P, Be, and O atoms. The model of the babefphite structure was refined by the block-diagonal approximation method with fixed positional parameters of the Ba_1 and Ba_2 atoms; this led to R_{hkl} = 10% with satisfactory B_j for all the atoms except two O atoms which occupied special one-parameter positions (00z) and (¼¼z). Furthermore, we fixed the shortened distances P–O and Be–O and a number of O–O edges in the PO_4 and BeO_4 tetrahedra. For more accurate location of the O atoms we constructed an electron density difference synthesis, on which we revealed splitting of the peaks corresponding to the position of these O, i.e., to their shift from the L_2 axis. Geometric analysis and calculation of the interatomic distances revealed that with a decrease in the symmetry of F1 and with selection of one of these peaks we obtain very satisfactory P–O, Be–O, and O–O distances in the PO_4 and BeO_4 tetrahedra. Furthermore, if we keep within the context of the space group F112, the babefphite structure will have [P_2O_7] groups with a bridging O atom on the L_2 (00z) axis, and [Be_2O_7] groups with a common O atom also on the L_2 (¼ ¼ z) axis. On the first O atom incorporated in the PO_4 tetrahedron the balance of the valence forces will be supersaturated ($\Sigma^+ = 5/4 + 5/4 + 2/9 = 2.72$), whereas on the second O atom incorporated into two Be tetrahedra and one Ba polyhedron the balance is undersaturated ($\Sigma^+ = 2/4 + 2/4 + 2/9 = 1.22$). With a decrease in the symmetry to F1 we have the possibility of convergence of the forces from one Be, one P and Ba on these O atoms; in this connection we attain a virtually ideal Pauling balance of the valence forces ($\Sigma^+ = 2/4 + 5/4 + 2/9 = 1.97$) [ideal for c. n. (BA) = 8]. Thus all this evidence confirms the trinclinic symmetry of the mineral, established from the x-ray oscillation photographs, and the subsequent determination of the crystal structure of babefphite was performed in the context of the space group F1.

On the basis of the previously refined atomic coordinates obtained in the context of the space group F112, taking account of the shift of some of the O atoms from the L_2 axes we constructed the three-dimensional electron density distribution, from which we located the deficient O, P, and Be atoms; in the location of the latter we allowed for the necessity to attain a satisfactory balance of the forces on the bridging O atoms common to the two tetrahedra. Refinement of the model of the structure of

TABLE III. Interatomic Distances in the Structure of Babefphite BaBe[PO$_4$]F (in ångstroms)

Ba$_1$- polyhedron	Ba$_2$- polyhedron	Be$_1$- tetrahedron	Be$_2$-tetrahedron
$\mathrm{Ba_1{-}O_1}$ =2.887(6)	$\mathrm{Ba_2{-}O_1}$ =2.982(7)	$\mathrm{Be_1{-}O_3}$=1.60(1)	$\mathrm{Be_2{-}O_2}$=1.63(1)
$\mathrm{{-}O_1'}$ =2.917(6)	$\mathrm{{-}O_3}$ =2.733(6)	$\mathrm{{-}O_6}$=1.62(1)	$\mathrm{{-}O_4}$=1.66(1)
$\mathrm{{-}O_2}$ =2.743(6)	$\mathrm{{-}O_4}$ =2.793(6)	$\mathrm{{-}O_7}$=1.69(1)	$\mathrm{{-}O_8}$=1.62(1)
$\mathrm{{-}O_5}$ =2.989(6)	$\mathrm{{-}O_5}$ =2.881(6)	$\mathrm{{-}F_1}$=1.53(1)	$\mathrm{{-}F_2}$=1.53(1)
$\mathrm{{-}O_7}$ =2.784(6)	$\mathrm{{-}O_5'}$ =2.920(6)	av 1.61	av. 1.61
$\mathrm{{-}O_8}$ =2.789(6)	$\mathrm{{-}O_6}$ =2.803(6)		
$\mathrm{{-}F_1}$ =3.036(6)	$\mathrm{{-}F_1}$ =2.869(6)	$\mathrm{O_3{-}O_6}$=2.665(9)	$\mathrm{O_2{-}O_4}$=2.639(8)
$\mathrm{{-}F_2}$ =2.872(5)	$\mathrm{{-}F_1'}$ =2.859(6)	$\mathrm{{-}O_7}$=2.640(8)	$\mathrm{{-}O_8}$=2.654(9)
$\mathrm{{-}F_2'}$ =2.863(6)	$\mathrm{{-}F_2}$ =3.020(6)	$\mathrm{{-}F_1}$=2.566(8)	$\mathrm{{-}F_2}$=2.571(8)
av 2.876	av 2.873	$\mathrm{O_6{-}O_7}$=2.657(8)	$\mathrm{O_4{-}O_8}$=2.504(9)
		$\mathrm{{-}F_1}$=2.594(8)	$\mathrm{{-}F_2}$=2.629(8)
$\mathrm{O_1{-}O_2}$ =3.096(9)	$\mathrm{O_1{-}O_3}$ =4.442(9)	$\mathrm{O_7{-}F_1}$=2.637(8)	$\mathrm{O_8{-}F_2}$=2.599(8)
$\mathrm{{-}O_8}$ =3.061(9)	$\mathrm{{-}O_5'}$ =4.586(9)	av. 2.626	av. 2.599
$\mathrm{{-}F_1}$ =2.907(9) *	$\mathrm{{-}O_6}$ =3.199(9)		
$\mathrm{{-}F_2'}$ =3.496(9)	$\mathrm{{-}F_1}$ =2.918(9) *	P$_1$- tetrahedron	P$_2$- tetrahedron
$\mathrm{O_1'{-}O_5}$ =4.590(9)	$\mathrm{{-}F_1'}$ =2.907(9) *		
$\mathrm{{-}O_7}$ =3.179(9)	$\mathrm{O_3{-}O_4}$ =3.383(9)	$\mathrm{P_1{-}O_1}$=1.512(7)	$\mathrm{P_2{-}O_3}$=1.560(6)
$\mathrm{{-}F_1}$ =2.918(9) *	$\mathrm{{-}O_5}$ =3.096(9)	$\mathrm{{-}O_2}$=1.551(6)	$\mathrm{{-}O_4}$=1.540(6)
$\mathrm{{-}F_2'}$ =4.511(9)	$\mathrm{{-}O_6}$ =3.355(9)	$\mathrm{{-}O_6}$=1.541(6)	$\mathrm{{-}O_5}$=1.504(6)
$\mathrm{{-}F_2'}$ =3.496(9)	$\mathrm{{-}F_1}$ =3.071(8)	$\mathrm{{-}O_7}$=1.541(6)	$\mathrm{{-}O_8}$=1.561(6)
$\mathrm{O_2{-}O_5}$ =4.463(9)	$\mathrm{{-}F_2}$ =4.426(9)	av. 1.536	av. 1.541
$\mathrm{{-}O_7}$ =3.377(8)	$\mathrm{O_4{-}O_5'}$ =3.186(8)		
$\mathrm{{-}O_8}$ =3.360(9)	$\mathrm{{-}F_1}$ =2.981(9)	$\mathrm{O_1{-}O_2}$=2.512(9)	$\mathrm{O_3{-}O_4}$=2.508(9)
$\mathrm{{-}F_1}$ =4.436(9)	$\mathrm{{-}F_2}$ =3.236(8)	$\mathrm{{-}O_6}$=2.525(9)	$\mathrm{{-}O_5}$=2.516(9)
$\mathrm{{-}F_2}$ =3.081(8)	$\mathrm{O_5{-}O_6}$ =3.067(9)	$\mathrm{{-}O_7}$=2.522(8)	$\mathrm{{-}O_8}$=2.512(8)
$\mathrm{O_5{-}O_8}$ =3.200(9)	$\mathrm{{-}F_1'}$ =4.428(9)	$\mathrm{O_2{-}O_6}$=2.492(8)	$\mathrm{O_4{-}O_5}$=2.521(8)
$\mathrm{{-}F_2}$ =2.919(8) *	$\mathrm{{-}F_2}$ =2.899(8) *	$\mathrm{{-}O_7}$=2.493(8)	$\mathrm{{-}O_8}$=2.658(9)
$\mathrm{{-}F_2'}$ =2.899(8) *	$\mathrm{O_5'{-}F_1}$ =4.507(9)	$\mathrm{O_6{-}O_7}$=2.657(8)	$\mathrm{O_5{-}O_8}$=2.537(9)
$\mathrm{O_7{-}F_1}$ =4.471(8)	$\mathrm{{-}F_1'}$ =3.484(9)	av. 2.534	av. 2.542
$\mathrm{{-}F_2}$ =2.979(8)	$\mathrm{{-}F_2}$ =2.919(8) *		
$\mathrm{O_8{-}F_2'}$ =3.198(8)	$\mathrm{O_6{-}F_1'}$ =3.213(8)		
$\mathrm{F_1{-}F_2'}$ =4.582(9)	$\mathrm{F_1{-}F_2}$ =4.564(8)		
av. 3.534	av. 3.517		

*Common edges of the Ba$_1$ and Ba$_2$ polyhedra.

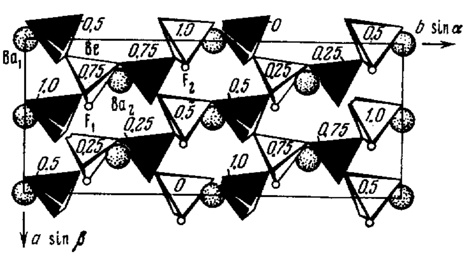

FIG. 1. Babefphite BaBe[PO$_4$]F. Projection on xy.

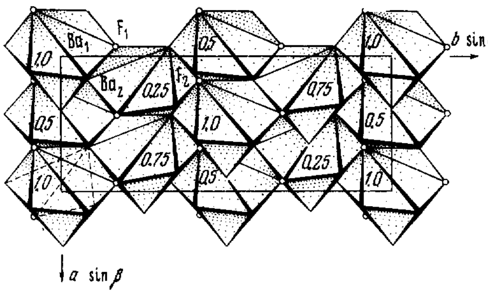

FIG. 2. Babefphite BaBe[PO$_4$]F. Projection on xy. Method of combination of the Ba nine-pointed polyhedra.

babefphite by MLS with use of the atomic scattering curve of oxygen for all the anions was performed to $R_{hkl} = 5.7\%$. Our analysis of the balance of the valence forces (Table I) enabled us to reveal two anions, for which there is an overall valence equivalent $\Sigma^+ = 1.17$. In accordance with this they were identified with two F atoms. Replacement of the atomic scattering curves for these anions by f-curves of F led to $R_{hkl} = 5.6\%$ in the isotropic approximation and to $R_{hkl} = 4.1\%$ in the anisotropic approximation, respectively. The final coordinates of the basis atoms, the individual isotropic and anisotropic corrections, and their corresponding interatomic distances are given in Tables II and III. From Table III we clearly see that the correctness of the separation of Be and P is also corroborated by the corresponding values of the cation–anion interatomic distances: Be–O(F) 1.53–1.69, av. 1.61 Å; P–O 1.504–1.561, av. 1.538 Å. The two types of Ba atoms are located in nine-pointed polyhedra [Ba$_1$–O(F) 2.743–3.036, Ba$_2$–O(F) 2.733–3.020 Å] and, being joined by common edges, they create a three-dimensional framework (Fig. 1), to which a mixed framework of P and Be tetrahedra corresponds (Fig. 2). The P and Be tetrahedra are joined at the vertices by closure of the P, Be pairs on the edge of the Ba nine-pointed polyhedron.

A comparison of these coordinates of the basis atoms and those previously obtained in the context of the space group Fdd2 (Ref. 1) revealed that in the selected arrangement (F1) the *a* and c axes change places.

According to the interpreted structure, with assignment of Be to the cation part the mineral babefphite must be regarded as an orthophosphate with the structural formula BaBe(PO$_4$)F (Z = 8).

In conclusion we thank E. P. Zhelezin for helping to obtain the experimental data, and also S. S. Meshalkin for assistance in selecting the single crystal.

1)Conversion to a standard primitive triclinic cell P1 can be effected from the matrix $\begin{pmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 1/2 & 1/2 \end{pmatrix}$, the axes of the P cell are selected from the diagonals of the *ab* and bc faces and are as follows: $a = 9.100(5)$; $b = 9.078(5)$; $c = 9.085(4)$ Å; $\alpha = 148.83(2)$; $\beta = 148.85(3)$; $\gamma = 44.60(4)°$.

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