**Supplementary Material**

**Fluoralforsite, Ba5(PO4)3F – a new barium mineral from the Hatrurim Basin, Negev Desert, Israel**

Arkadiusz Krzątała1, Katarzyna Skrzyńska\*1, Georgia Cametti2, Irina Galuskina1, Yevgeny Vapnik3 and Evgeny Galuskin1

*1Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland*

*2* *Institute of Geological Sciences,* *University of Bern, Baltzerstrasse 1+3, 3012 Bern, Switzerland*

*3Department of Geological and Environmental Sciences, Ben-Gurion University of the Negev, POB 653, Beer-Sheva 84105, Israel*

\*Email: katarzyna.skrzynska@us.edu.pl

**S1 Structure refinement of fluoralforstie in space group *P*63**

The structure of fluoralforstie was refined in space groups *P*63 for test purposes. Data collection and structural parameters are reported in Table S1 and S2, respectively. The cationic and oxygen sites, related by the mirror plane in *P*63/*m* space group, are labelled as *M*1 and *M*1’ and O3 and O3’, respectively. The refinement in space group *P*63 and the analysis of the intensities distribution clearly pointed to a centric space group. The occupancy of *M*1 and *M*1’ sites, related by the mirror plane in *P*63/*m*, converged to very similar values of Ca vs Ba (Table S2a), although a slight preference for Ca at *M*1A and Ba at *M*1’, can be noticed.

**Table S1** Data collection and crystal-structure refinement parameters of fluoralforsite in space group *P*63

|  |  |
| --- | --- |
| **crystal data** | |
| Empirical formula | Ba4.03Ca0.97 (P2.80V0.20)O12(F0.90Cl0.12) |
| Refined chemical formula | Ba4Ca0.99 P3O12(F0.55Cl0.26) |
| Crystal system | Hexagonal |
| Space group | *P*63 |
| Unit cell dimensions [Å.°] | *a* = 10.0031(2) |
| *c* = 7.5382(2) |
| *γ* = 120° |
| Volume [Å3] | 653.23(3) |
| Z | 2 |
| Formula weight | 895.48 |
| Density (calculated) [g/cm3] | 4.553 |
| Crystal size [mm] | 0.05×0.04×0.03 |
| **data collection** | |
| Diffractometer | Rigaku XtaLAB, Synergy R |
| Radiation wavelength [Å] | 0.71073 |
| Detector to sample distance [mm] | 50 |
| Temperature [K] | 293(2) |
| Total time/Dose time | 1h 18m/ 1h 16m |
| *F*(000) | 790 |
| *θ* range for data collection [°] | 2.35-35.064 |
| Index ranges | -15 ≤ h ≤ 15  -15≤ k ≤ 16  -11≤ l ≤12 |
| Reflections collected | 17386 |
| Independent reflections | 1009 |
| Observed Data [*I*>2σ(*I*)] | 890 |
| *R*int and *R*sigma | 0.0543 and 0.0274 |
| **refinement** | |
| No. parameters | 92 |
| No. of restraints | 1 |
| Weighting scheme | *w* = 1/[σ2(*F*o2) + (0.0241*P*)2 + 0.00*P*]  where *P* = (*F*o2 + 2*F*c2)/3 |
| *R*1. w*R*2 [*I*>2σ(*I*)] | 0.0214; 0.0464 |
| *R*1. w*R*2 (for all) | 0.0284; 0.0483 |
| GooF | 1.024 |
| Refined as inversion twin |  |
| BASF | 0.52(7) |
| Δρmin [e/Å -3] close to | -0.71 O3A |
| Δρmax [e/Å -3] close to | 0.91 O1 |

**Table S2** Atom coordinates, equivalent isotropic or isotropic (\*) displacement parameters, and site occupancies of fluoralforsite in space group *P*63

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Site** | **Atom** | ***x*** | ***y*** | ***z*** | ***Ueq/Uiso*[Å2]** | **occupancy** |
| M2 | Ba | 0.25419(5) | 0.01918(5) | 0.1903(4) | 0.0172(3) | 0.874(14) |
| M2A | Ba | 0.2516(9) | 0.0167(8) | 0.216(3) | 0.06\* | 0.126(14) |
| M1 | Ba | 0.6667 | 0.3333 | 0.44459(10) | 0.0172(7) | 0.460(6) |
| M1A | Ca | 0.6667 | 0.3333 | 0.44459(10) | 0.0172(7) | 0.539(6) |
| M1’ | Ba | 0.6667 | 0.3333 | -0.06008(6) | 0.0193(7) | 0.553(6) |
| M1’A | Ca | 0.6667 | 0.3333 | -0.06008(6) | 0.0193(7) | 0.446(6) |
| P1 | P | 0.02856(10) | -0.37884(10) | 0.1899(10) | 0.0155(2) | 1 |
| O1 | O | 0.5025(4) | 0.3586(4) | 0.191(2) | 0.0437(11) | 1 |
| O2 | O | 0.4162(18) | -0.134(2) | 0.144(4) | 0.013(3) | 0.43(5) |
| O2A | O | 0.416(2) | -0.122(2) | 0.217(3) | 0.027(5)\* | 0.57(5) |
| O3’ | O | 0.2730(11) | 0.3430(18) | 0.0310(19) | 0.047(4) | 1 |
| O3 | O | 0.368(4) | 0.085(3) | -0.136(3) | 0.024(4) | 0.56(13) |
| O3A | O | 0.315(8) | 0.047(6) | -0.155(5) | 0.034(7) | 0.44(13) |
| Cl | Cl | 0 | 0 | 0.059(4) | 0.046(5)\* | 0.27(2) |
| F1 | F | 0 | 0 | -0.029(4) | 0.015(6)\* | 0.21(3) |
| F | F | 0 | 0 | 0.138(4) | 0.025(6)\* | 0.33(4) |

**S2 Structure refinement of fluoralforstie in space group *P***

In order to test eventual symmetry lowering, test refinement was performed in space group *P*. Data collection details and structural parameters are provided in Tables S3 an S4, respectively. Two independent *M*1 and *M*11 sites revealed a mixed occupancy of Ba and Ca. No evidence of the ordering of Ba and Ca at *M*1 polyhedra can be observed.

**Table S3** Data collection and crystal-structure refinement parameters of fluoralforsite in space group *P*

|  |  |
| --- | --- |
| **crystal data** | |
| Empirical formula | Ba4.03Ca0.97 (P2.80V0.20)O12(F0.90Cl0.12) |
| Refined chemical formula | Ba4.00Ca1.01 (P2.80V0.20)O12(F0.83Cl0.136) |
| Crystal system | trigonal |
| Space group | *P* |
| Unit cell dimensions [Å.°] | *a* = 10.0031(2) |
| *c* = 7.5382(2) |
| *γ* = 120° |
| Volume [Å3] | 653.23(3) |
| Z | 2 |
| Formula weight | 898.415 |
| Density (calculated) [g/cm3] | 4.568 |
| Crystal size [mm] | 0.05×0.04×0.03 |
| **data collection** | |
| Diffractometer | Rigaku XtaLAB, Synergy R |
| Radiation wavelength [Å] | 0.71073 |
| Detector to sample distance [mm] | 50 |
| Temperature [K] | 293(2) |
| Total time/Dose time | 1h 18m/ 1h 16m |
| *F*(000) | 790 |
| *θ* range for data collection [°] | 2.35-35.064 |
| Index ranges | -15 ≤ h ≤ 15  -15≤ k ≤ 16  -11≤ l ≤12 |
| Reflections collected | 17386 |
| Independent reflections | 1009 |
| Observed Data [*I*>2σ(*I*)] | 890 |
| *R*int and *R*sigma | 0.0518 and 0.0263 |
| **refinement** | |
| No. parameters | 80 |
| No. of restraints | 0 |
| Weighting scheme | *w* = 1/[σ2(*F*o2) + (0.0253*P*)2 + 1.3655*P*]  where *P* = (*F*o2 + 2*F*c2)/3 |
| *R*1. w*R*2 [*I*>2σ(*I*)] | 0.0269; 0.0585 |
| *R*1. w*R*2 (for all) | 0.0342; 0.0608 |
| GooF | 1.068 |
| Δρmin [e/Å -3] | -1.113 |
| Δρmax [e/Å -3] | 1.381 |

**Table S4** Atom coordinates, equivalent isotropic or isotropic (\*) displacement parameters, and site occupancies of fluoralforsite in space group *P*

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **site** | **atom** | ***x*** | ***y*** | ***z*** | ***Ueq/Uiso\**[Å2]** | **occupancy** |
| M2 | Ba | 0.25412(3) | 0.01911(3) | 0.75004(3) | 0.01895(17) | 0.929(6) |
| M2A | Ba | 0.243(3) | 0.014(2) | 0.749(2) | 0.158(19)\* | 0.071(6) |
| M1 | Ba | 0.6667 | 0.3333 | 0.49761(7) | 0.01865(13) | 0.498(3) |
| M1A | Ca | 0.6667 | 0.3333 | 0.49761(7) | 0.01865(13) | 0.501(3) |
| M11 | Ba | 0.6667 | 0.3333 | 1.00233(6) | 0.01855(12) | 0.498(3) |
| M11A | Ca | 0.6667 | 0.3333 | 1.00233(6) | 0.01855(12) | 0.501(3) |
| P1 | P | 0.02867(9) | -0.37872(9) | 0.75012(11) | 0.01754(18) | 0.934 |
| V1 | V | 0.02867(9) | -0.37872(9) | 0.75012(11) | 0.01754(18) | 0.066 |
| O1 | O | 0.5027(3) | 0.3585(4) | 0.7500(5) | 0.0431(8) | 1 |
| O2 | O | 0.3458(5) | 0.0712(4) | 1.0867(4) | 0.0504(10) | 1 |
| O3 | O | 0.3463(5) | 0.0714(5) | 0.4136(4) | 0.0508(10) | 1 |
| O4 | O | 0.1279(4) | -0.4563(4) | 0.7499(6) | 0.0576(11) | 1 |
| F1 | F | 0.0000 | 0.0000 | 0.883(3) | 0.030(6)\* | 0.25(2) |
| F2 | F | 0.0000 | 0.0000 | 0.782(5) | 0.053(9)\* | 0.24(3) |
| F3 | F | 0.0000 | 0.0000 | 0.640(2) | 0.046(5)\* | 0.34(2) |
| Cl1 | Cl | 0.0000 | 0.0000 | 0.5000 | 0.059(9)\* | 0.151(15) |
| Cl2 | Cl | 0.0000 | 0.0000 | 1.0000 | 0.047(9)\* | 0.121(15) |

**S3 Structure refinement of fluoralforstie in space group *P*21*/m***

An additional structural refinement was performed in space group *P*21/*m*. Details of data acquisition and structural parameters are reported in Table S5 and S6, respectively. M2 position exhibits high disorder, which was difficult to model due to high correlation between pseudo-symmetry related sites. Overall, the quality of the structural refinement clearly pointed to a higher symmetry space group.

**Table S5** Data collection and crystal-structure refinement parameters of fluoralforsite in space group *P*21*/m*

|  |  |
| --- | --- |
| **crystal data** | |
| Empirical formula | Ba4.03Ca0.97 (P2.80V0.20)O12(F0.90Cl0.12) |
| Refined chemical formula | Ba4.06Ca0.945 (P2.74V0.26)O12(F0.89Cl0.165) |
| Crystal system | monoclinic |
| Space group | *P*21*/m* |
| Unit cell dimensions [Å.°] | *a* = 10.0031(2) |
| *c* = 7.5382(2) |
| *γ* = 120° |
| Volume [Å3] | 653.23(5) |
| Z | 2 |
| Formula weight | 907.65 |
| Density (calculated) [g/cm3] | 4.615 |
| Crystal size [mm] | 0.05×0.04×0.03 |
| **data collection** | |
| Diffractometer | Rigaku XtaLAB, Synergy R |
| Radiation wavelength [Å] | 0.71073 |
| Detector to sample distance [mm] | 50 |
| Temperature [K] | 293(2) |
| Total time/Dose time | 1h 18m/ 1h 16m |
| *F*(000) | 790 |
| *θ* range for data collection [°] | 2.35-35.064 |
| Index ranges | -15 ≤ h ≤ 15  -15≤ k ≤ 16  -11≤ l ≤12 |
| Reflections collected | 17386 |
| Independent reflections | 1009 |
| Observed Data [*I*>2σ(*I*)] | 890 |
| *R*int and *R*sigma | 0.0451 and 0.0306 |
| **refinement** | |
| No. parameters | 127 |
| No. of restraints | 0 |
| Weighting scheme | *w* = 1/[σ2(*F*o2) + (0.0447*P*)2 + 0.738 *P*]  where *P* = (*F*o2 + 2*F*c2)/3 |
| *R*1. w*R*2 [*I*>2σ(*I*)] | 0.0318; 0.0829 |
| *R*1. w*R*2 (for all) | 0.0402; 0.0857 |
| GooF | 1.169 |
| Δρmin [e/Å -3] | -1.906 |
| Δρmax [e/Å -3] | 1.967 |

**Table S6** Atom coordinates, equivalent isotropic or isotropic (\*) displacement parameters, and site occupancies of fluoralforsite in space group *P*21*/m*

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **site** | **atom** | ***x*** | ***y*** | ***z*** | ***Ueq/Uiso\**[Å2]** | **occupancy** |
| M1 | Ba | 0.83324(4) | -0.00240(5) | 0.66665(4) | 0.01847(11) | 0.527(2) |
| M1A | Ca | 0.83324(4) | -0.00240(5) | 0.66665(4) | 0.01847(11) | 0.473(2) |
| M2 | Ba | 0.51909(4) | 0.2500 | 0.76504(4) | 0.02024(9) | 1 |
| M21 | Ba | 0.24602(4) | 0.2500 | 0.98099(4) | 0.02027(9) | 1 |
| M23 | Ba | 0.73520(12) | 0.2500 | 1.25426(13) | 0.0196(2) | 0.982(7) |
| M23A | Ba | 0.697(10) | 0.2500 | 1.213(11) | 0.049(14)*\** | 0.018(7) |
| P1 | P | 0.90741(15) | 0.2500 | 1.02894(14) | 0.0163(3) | 0.922(8) |
| P1A | V | 0.90741(15) | 0.2500 | 1.02894(14) | 0.0163(3) | 0.078(8) |
| P2 | P | 0.47130(15) | 0.2500 | 0.37870(14) | 0.0163(3) | 0.922(8) |
| P2A | V | 0.47130(15) | 0.2500 | 0.37870(14) | 0.0163(3) | 0.078(8) |
| P3 | P | 0.12132(15) | 0.2500 | 0.59276(15) | 0.0169(3) | 0.895(11) |
| P3A | V | 0.12132(15) | 0.2500 | 0.59276(15) | 0.0169(3) | 0.105(11) |
| O1 | O | 0.8572(6) | 0.2500 | 0.8548(5) | 0.0408(13) | 1 |
| O2 | O | -0.0020(5) | 0.2500 | 0.6423(6) | 0.0411(13) | 1 |
| O3 | O | 0.6449(5) | 0.2500 | 1.5025(5) | 0.0421(14) | 1 |
| O4 | O | 0.5717(5) | -0.0863(5) | 0.7252(4) | 0.0484(11) | 1 |
| O5 | O | 0.2248(4) | 0.0861(5) | 0.6537(5) | 0.0477(11) | 1 |
| O6 | O | 0.1542(5) | -0.0869(5) | 0.9288(5) | 0.0473(11) | 1 |
| O7 | O | 1.0842(6) | 0.2500 | 1.1281(6) | 0.0564(19) | 1 |
| O8 | O | 0.3720(6) | 0.2500 | 0.4562(6) | 0.0560(19) | 1 |
| O9 | O | 0.0434(6) | 0.2500 | 0.4162(6) | 0.0558(18) | 1 |
| F | F | 0.4994(11) | 0.1315(17) | 1.0005(11) | 0.037(4)\* | 0.316(14) |
| F1 | F | 0.498(3) | 0.2500 | 1.002(2) | 0.058(10)\* | 0.26(3) |
| Cl | Cl | 0.5000 | 0.0000 | 1.0000 | 0.059(6)\* | 0.162(12) |