**Table S1.** Atomic coordinates, displacement parameters (Å2), and bond valence sums for paddlewheelite.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Atom** | **Occ.** | **x** | **y** | **z** | **Ueq/Uiso** | **BVS** | **Atom** | **Occ.** | | **x** | **y** | **z** | | **Ueq/Uiso** |
| U1 | 1 | 0.68153(7) | 0.73822(9) | 0.80002(9) | 0.0277(5) | 6.00 | O16 | 1 | 0.9972(11) | | 0.5674(14) | 1.6984(13) | 0.021(6) | |
| U2 | 1 | 1.00180(8) | −0.34143(8) | 1.50185(8) | 0.0201(4) | 6.41 | O17 | 1 | 0.4976(13) | | 0.2279(16) | 1.1850(14) | 0.031(7) | |
| U3 | 1 | 0.49882(8) | 0.34218(9) | 1.10900(7) | 0.0243(4) | 6.28 | O18 | 1 | 0.5782(13) | | 0.3449(17) | 1.1087(16) | 0.035(8) | |
| U4 | 1 | 1.01776(8) | 0.15786(9) | 1.61252(8) | 0.0267(5) | 6.02 | O19 | 1 | 0.6731(12) | | 0.6091(16) | 0.8478(14) | 0.031(7) | |
| U5 | 1 | 0.50127(8) | −0.15833(8) | 0.99888(8) | 0.0223(4) | 6.38 | O20 | 1 | 0.4194(14) | | 0.3401(18) | 1.1113(17) | 0.045(9) | |
| U6 | 1 | 0.82387(7) | −0.23572(9) | 1.29408(9) | 0.0264(5) | 6.11 | O21 | 1 | 1.1941(14) | | −0.2289(18) | 1.2321(16) | 0.040(8) | |
| U7 | 1 | 1.19072(7) | −0.26464(10) | 1.31566(9) | 0.0243(4) | 6.35 | O22 | 1 | 0.5074(10) | | −0.0688(13) | 1.1951(12) | 0.016(6) | |
| U8 | 1 | 1.31450(8) | 0.75641(10) | 0.79086(11) | 0.0396(6) | 6.72 | O23 | 1 | 0.5092(11) | | 0.0113(15) | 1.3305(14) | 0.019(6) | |
| Cu1 | 1 | 0.4949(2) | 0.5529(3) | 0.8727(2) | 0.0146(11) | 2.11 | O24 | 1 | 1.0863(10) | | 0.4527(13) | 1.7522(12) | 0.014(6) | |
| Cu2 | 1 | 1.0123(2) | −0.0534(3) | 1.3753(2) | 0.0139(11) | 2.08 | O25 | 1 | 1.0964(12) | | 0.3262(16) | 1.7816(15) | 0.028(7) | |
| Cu3 | 1 | 0.9992(2) | 0.4462(3) | 1.7391(3) | 0.0162(11) | 2.01 | O26 | 1 | 0.4756(11) | | −0.3310(15) | 1.3080(13) | 0.026(6) | |
| Cu4 | 1 | 0.5029(2) | 0.0531(3) | 1.2367(3) | 0.0175(11) | 1.97 | O27 | 1 | 1.0003(12) | | −0.2286(15) | 1.4282(14) | 0.022(6) | |
| Ca1 | 1 | 0.4989(4) | 0.7495(5) | 0.8047(5) | 0.0151(16) | 2.42 | O28 | 1 | 0.5051(11) | | −0.0528(15) | 1.0815(13) | 0.023(6) | |
| Ca2 | 1 | 1.0068(4) | 0.2508(5) | 1.8074(4) | 0.0112(15) | 2.42 | O29 | 1 | 0.9884(11) | | 0.6693(14) | 0.8007(12) | 0.020(6) | |
| Ca3 | 1 | 1.0351(5) | −0.0725(5) | 1.5861(5) | 0.042(3) | 2.16 | O30 | 1 | 0.5820(12) | | 0.5518(15) | 0.8781(14) | 0.029(7) | |
| Ca4 | 1 | 1.0111(5) | 0.4297(5) | 1.5280(4) | 0.040(3) | 2.15 | O31 | 1 | 1.1000(13) | | −0.1881(17) | 1.3318(15) | 0.032(7) | |
| Ca5 | 1 | 0.5088(5) | −0.0717(5) | 1.5233(4) | 0.031(2) | 2.19 | O32 | 1 | 0.5023(13) | | 0.1316(17) | 1.3769(15) | 0.033(7) | |
| Ca6 | 1 | 0.4796(4) | 0.4293(4) | 0.5831(4) | 0.026(2) | 2.12 | O33 | 1 | 0.7824(11) | | 0.7875(14) | 0.7753(13) | 0.023(6) | |
| Ca7 | 1 | 0.7415(4) | −0.0399(5) | 1.3603(5) | 0.035(2) | 2.36 | O34 | 1 | 0.4997(12) | | 0.5101(15) | 0.7788(14) | 0.026(7) | |
| Ca8 | 1 | 0.7662(4) | 0.5411(4) | 1.8667(5) | 0.038(2) | 2.16 | O35 | 1 | 0.5918(12) | | 0.1854(16) | 1.2778(14) | 0.026(7) | |
| Ca9 | 1 | 1.2789(4) | −0.0707(4) | 1.3839(4) | 0.029(2) | 2.09 | O36 | 1 | 0.4868(11) | | 0.4343(13) | 0.9137(12) | 0.016(6) | |
| Ca10 | 1 | 0.2252(4) | 0.5607(5) | 0.8503(7) | 0.057(3) | 1.99 | O37 | 1 | 1.0205(12) | | 0.0495(16) | 1.5335(14) | 0.029(7) | |
| Mg2 | 1 | 0.5602(6) | −0.2768(6) | 1.2931(6) | 0.015(3) | 2.10 | O38 | 1 | 0.9872(11) | | 0.4884(14) | 1.8348(12) | 0.020(6) | |
| Mg1 | 1 | 0.9456(6) | 0.7773(7) | 0.8001(6) | 0.022(3) | 2.08 | O39 | 1 | 1.1860(13) | | −0.1292(17) | 1.3586(15) | 0.033(7) | |
| O1 | 1 | 1.3194(15) | 0.7143(18) | 0.7062(16) | 0.046(9) |  | O40 | 1 | 0.9123(13) | | 0.8904(18) | 0.7934(15) | 0.044(8) | |
| O2 | 1 | 0.5927(12) | 0.0629(16) | 1.2337(14) | 0.028(7) |  | O41 | 1 | 0.9226(13) | | −0.3316(16) | 1.5048(15) | 0.033(7) | |
| O3 | 1 | 0.9919(11) | 0.4695(14) | 1.9476(13) | 0.020(6) |  | O42 | 1 | 0.4954(12) | | 0.7289(14) | 0.9246(12) | 0.019(6) | |
| O4 | 1 | 1.0100(10) | 0.3941(13) | 1.6487(12) | 0.011(5) |  | O43 | 1 | 0.6384(12) | | −0.2133(15) | 1.2837(14) | 0.029(6) | |
| O5 | 1 | 0.4958(11) | 0.1048(13) | 1.1470(12) | 0.018(6) |  | O44 | 1 | 0.8273(12) | | 0.3648(15) | 1.7435(13) | 0.025(6) | |
| O6 | 1 | 0.9362(14) | 0.1533(18) | 1.6091(17) | 0.041(9) |  | O45 | 1 | 0.5508(11) | | −0.2794(14) | 1.1885(12) | 0.025(6) | |
| O7 | 1 | 0.5119(12) | 0.0315(16) | 1.4461(15) | 0.030(7) |  | O46 | 1 | 0.9195(13) | | −0.1688(18) | 1.3235(16) | 0.037(8) | |
| O8 | 1 | 0.6846(14) | 0.7818(18) | 0.8874(16) | 0.040(8) |  | O47 | 1 | 1.0248(11) | | 0.0638(14) | 1.4180(13) | 0.021(6) | |
| O9 | 1 | 0.9988(12) | 0.3679(15) | 1.8787(14) | 0.020(6) |  | O48 | 1 | 0.5864(14) | | 0.4143(18) | 0.6013(16) | 0.052(9) | |
| O10 | 1 | 1.0149(11) | −0.2042(14) | 1.5391(13) | 0.021(6) |  | O49 | 1 | 0.4096(12) | | 0.1747(16) | 1.2726(14) | 0.028(7) | |
| O11 | 1 | 1.1006(12) | −0.0617(16) | 1.3686(14) | 0.027(7) |  | O50 | 1 | 0.9146(12) | | 0.3126(16) | 1.7682(15) | 0.032(7) | |
| O12 | 1 | 0.6783(13) | 0.1294(17) | 1.2526(15) | 0.036(8) |  | O51 | 1 | 1.3370(12) | | 0.0432(16) | 1.4162(14) | 0.033(7) | |
| O13 | 1 | 0.4927(12) | 0.7035(15) | 1.0368(13) | 0.026(7) |  | O52 | 1 | 0.5008(13) | | 0.6297(18) | 0.7336(15) | 0.035(8) | |
| O14 | 1 | 1.1890(12) | −0.3022(16) | 1.4010(14) | 0.028(7) |  | O53 | 1 | 1.1809(12) | | 0.3977(15) | 1.7770(14) | 0.029(7) | |
| O15 | 1 | 0.4964(12) | 0.3341(14) | 0.9853(13) | 0.024(6) |  | O54 | 1 | 1.2180(12) | | 0.6910(16) | 0.8022(14) | 0.032(7) | |

Table S1 (cont). Atomic coordinates, displacement parameters (Å2), and bond valence sums for paddlewheelite.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Atom** | **Occ.** | **x** | **y** | **z** | **Ueq/Uiso** | **Atom** | **Occ.** | **x** | **y** | **z** | **Ueq/Uiso** |
| O55 | 1 | 1.0101(13) | 0.2705(17) | 1.6889(15) | 0.032(7) | O94 | 1 | 0.3266(12) | 0.1138(15) | 1.2439(13) | 0.025(6) |
| O56 | 1 | 0.9376(12) | 0.7695(15) | 0.9081(14) | 0.034(7) | O95 | 1 | 0.4056(12) | 0.5578(16) | 0.8627(14) | 0.029(7) |
| O57 | 1 | 1.0125(12) | −0.1039(16) | 1.4672(14) | 0.026(7) | O96 | 1 | 1.0983(12) | 0.1607(15) | 1.6174(14) | 0.029(7) |
| O58 | 1 | 0.4062(12) | 0.6852(17) | 0.8233(15) | 0.030(7) | O97 | 1 | 0.6678(19) | −0.226(3) | 1.574(2) | 0.098(14) |
| O59 | 0.5 | 1.378(3) | −0.233(4) | 1.137(4) | 0.06(2) | O98 | 1 | 1.0809(13) | 0.8697(16) | 0.6852(14) | 0.040(7) |
| O60 | 1 | 0.4134(12) | 0.0483(15) | 1.2423(14) | 0.027(7) | O99 | 1 | 0.4997(12) | 0.5294(15) | 0.6655(13) | 0.022(6) |
| O61 | 1 | 0.5748(10) | −0.2722(13) | 1.4009(12) | 0.019(5) | O100 | 1 | 0.4600(12) | −0.1510(15) | 1.4313(14) | 0.036(7) |
| O62 | 1 | 1.0163(13) | −0.1310(17) | 1.2378(15) | 0.033(7) | O101 | 1 | 0.375(2) | 0.434(3) | 0.548(2) | 0.096(14) |
| O63 | 1 | 0.5864(11) | 0.6733(15) | 0.8285(13) | 0.022(6) | O102 | 1 | 0.6573(19) | 0.524(3) | 0.674(2) | 0.091(14) |
| O64 | 1 | 0.7328(12) | −0.1673(16) | 1.3081(14) | 0.033(7) | O103 | 1 | 0.8743(15) | 0.5743(19) | 0.8634(18) | 0.063(10) |
| O65 | 1 | 1.0088(11) | −0.0105(15) | 1.2844(14) | 0.026(7) | O104 | 1 | 1.3793(11) | −0.0866(14) | 1.3325(13) | 0.027(6) |
| O66 | 1 | 0.9928(11) | 0.5510(14) | 1.5817(13) | 0.019(6) | O105 | 1 | 0.5938(13) | −0.3915(16) | 1.2876(14) | 0.039(7) |
| O67 | 1 | 0.8362(13) | −0.1056(16) | 1.3490(14) | 0.032(7) | O106 | 1 | 0.6543(16) | 0.318(2) | 0.5140(19) | 0.070(11) |
| O68 | 1 | 0.4901(11) | 0.4490(13) | 1.0282(12) | 0.016(6) | O107 | 1 | 0.1193(13) | 0.5883(17) | 0.8199(15) | 0.041(8) |
| O69 | 1 | 1.0309(13) | 0.8296(16) | 0.8160(15) | 0.036(7) | O108 | 1 | 1.0183(12) | −0.0299(15) | 1.1698(14) | 0.026(7) |
| O70 | 1 | 0.4963(12) | −0.1683(14) | 1.1238(13) | 0.025(6) | O109 | 1 | 0.9300(13) | 0.0912(17) | 1.1073(15) | 0.045(8) |
| O71 | 1 | 0.7236(11) | −0.2850(14) | 1.2626(13) | 0.022(6) | O110 | 1 | 0.8536(16) | 0.183(2) | 1.0192(18) | 0.061(10) |
| O72 | 1 | 0.4912(12) | 0.6056(14) | 0.9630(13) | 0.024(6) | O111 | 1 | 0.9127(15) | 0.607(2) | 1.0014(18) | 0.065(10) |
| O73 | 1 | 0.6879(15) | 0.0607(19) | 1.4243(17) | 0.060(10) | O112 | 1 | 0.8182(14) | −0.2778(18) | 1.3792(16) | 0.041(8) |
| O74 | 1 | 1.2862(13) | −0.1986(18) | 1.3391(16) | 0.042(8) | O113 | 1 | 0.6780(12) | 0.6964(16) | 0.7158(14) | 0.034(7) |
| O75 | 1 | 0.7754(11) | 0.6730(14) | 0.8192(13) | 0.023(6) | O114 | 1 | 0.6367(14) | −0.0587(18) | 1.3294(16) | 0.052(8) |
| O76 | 1 | 1.0226(11) | 0.1673(14) | 1.4877(13) | 0.024(6) | O115 | 1 | 0.7314(19) | −0.107(3) | 1.464(2) | 0.089(14) |
| O77 | 1 | 0.9127(10) | 0.4337(14) | 1.7298(12) | 0.014(6) | O116 | 1 | 0.860(2) | −0.027(3) | 1.180(3) | 0.112(17) |
| O78 | 1 | 0.5019(12) | 0.2030(15) | 1.0744(14) | 0.026(7) | O117 | 1 | 0.8663(13) | 0.7172(16) | 0.7985(14) | 0.037(7) |
| O79 | 1 | 0.4033(11) | −0.0367(15) | 1.5298(13) | 0.030(6) | O118 | 1 | 1.2916(12) | −0.3173(15) | 1.2932(14) | 0.032(7) |
| O80 | 1 | 0.9516(12) | 0.7773(16) | 0.6942(14) | 0.037(7) | O119 | 1 | 0.3609(15) | −0.048(2) | 1.1411(18) | 0.065(10) |
| O81 | 1 | 0.4213(12) | −0.1497(16) | 0.9959(15) | 0.029(7) | O120 | 1 | 0.7618(19) | 0.610(3) | 1.972(2) | 0.093(13) |
| O82 | 1 | 1.3069(16) | 0.791(2) | 0.8683(18) | 0.060(10) | O121 | 1 | 0.3205(13) | 0.6273(16) | 0.8460(14) | 0.034(7) |
| O83 | 1 | 1.0087(11) | 0.6680(14) | 1.6236(13) | 0.019(6) | O122 | 1 | 1.1166(14) | 0.4666(18) | 1.5512(16) | 0.054(9) |
| O84 | 1 | 0.1740(14) | 0.4729(18) | 0.9283(16) | 0.049(9) | O123 | 1 | 1.0803(12) | −0.3497(16) | 1.5019(15) | 0.027(7) |
| O85 | 1 | 0.5795(12) | −0.1665(16) | 1.0039(15) | 0.029(7) | O124 | 0.3 | 0.656(4) | −0.091(5) | 1.164(4) | 0.03(2) |
| O86 | 1 | 1.0184(11) | 0.2955(15) | 1.5770(13) | 0.024(6) | O125 | 1 | 1.3031(15) | −0.134(2) | 1.4947(17) | 0.063(10) |
| O87 | 1 | 1.2177(16) | 0.810(2) | 0.7529(18) | 0.069(11) | O126 | 1 | 1.136(2) | −0.073(3) | 1.552(2) | 0.110(16) |
| O88 | 1 | 0.4269(13) | 0.3834(16) | 0.6819(14) | 0.038(7) | O127 | 1 | 0.8185(15) | 0.4388(19) | 1.9262(17) | 0.057(9) |
| O89 | 1 | 1.3752(13) | −0.2429(16) | 1.2999(15) | 0.038(7) | O128 | 1 | 0.2272(17) | 0.636(2) | 0.9540(19) | 0.075(11) |
| O90 | 1 | 0.5918(14) | −0.1203(19) | 1.4534(16) | 0.055(9) | O129 | 1 | 0.6885(18) | −0.316(2) | 1.448(2) | 0.085(12) |
| O91 | 1 | 1.128(2) | 0.733(2) | 0.754(2) | 0.088(13) | O130 | 1 | 0.3525(17) | 0.535(2) | 0.6908(19) | 0.073(11) |
| O92 | 1 | 0.9230(12) | −0.0518(15) | 1.3763(14) | 0.027(7) | O131 | 1 | 0.3044(14) | 0.4584(18) | 0.8650(16) | 0.051(9) |
| O93 | 1 | 0.5130(12) | −0.1724(17) | 1.2971(13) | 0.033(8) | O132 | 1 | 0.2394(15) | 0.534(2) | 0.7299(18) | 0.064(10) |

**Table S1 (cont).** Atomic coordinates, displacement parameters (Å2), and bond valence sums for paddlewheelite.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Atom** | **Occ.** | **x** | **y** | **z** | **Ueq/Uiso** | **Atom** | **Occ.** | **x** | **y** | **z** | **Ueq/Uiso** | **BVS** |
| O133 | 1 | 1.2549(14) | −0.0025(18) | 1.2821(16) | 0.053(9) | C1 | 1 | 0.379(2) | 0.624(3) | 0.844(2) | 0.042(12) | 3.90 |
| O134 | 0.7 | 0.680(3) | −0.487(4) | 1.447(3) | 0.090(19) | C2 | 1 | 1.186(3) | 0.742(3) | 0.771(2) | 0.062(15) | 3.56 |
| O135 | 0.8 | 0.851(2) | 0.727(3) | 1.071(3) | 0.100(18) | C3 | 1 | 0.892(2) | −0.108(3) | 1.350(3) | 0.049(14) | 4.11 |
| O136 | 1 | 0.6108(18) | −0.068(2) | 1.586(2) | 0.091(13) | C4 | 1 | 1.0126(16) | −0.055(2) | 1.233(2) | 0.018(9) | 3.94 |
| O137 | 1 | 0.365(2) | −0.270(3) | 1.481(2) | 0.108(15) | C5 | 1 | 1.1290(17) | −0.125(2) | 1.3533(19) | 0.017(9) | 3.94 |
| O138 | 1 | 0.7487(19) | 0.002(3) | 1.236(2) | 0.097(15) | C6 | 1 | 0.6926(18) | −0.225(2) | 1.285(2) | 0.023(9) | 3.84 |
| O139 | 1 | 1.2042(15) | 0.0020(19) | 1.4529(17) | 0.061(9) | C7 | 1 | 0.6155(18) | 0.613(2) | 0.854(2) | 0.022(9) | 3.66 |
| O140 | 0.5 | 0.820(3) | 0.979(4) | 0.930(4) | 0.07(2) | C8 | 1 | 0.4993(18) | 0.555(2) | 0.724(2) | 0.020(9) | 4.18 |
| O141 | 0.5 | 1.139(4) | 0.231(5) | 1.418(5) | 0.10(3) | C9 | 1 | 1.0132(16) | 0.320(2) | 1.6353(19) | 0.014(8) | 4.04 |
| O142 | 1 | 1.0582(13) | 0.3635(17) | 1.4344(15) | 0.045(8) | C10 | 1 | 0.8097(19) | 0.725(2) | 0.799(2) | 0.030(10) | 4.18 |
| O143 | 1 | 1.1445(19) | 0.593(3) | 1.641(2) | 0.097(14) | C11 | 1 | 1.0011(17) | 0.595(2) | 1.637(2) | 0.019(9) | 3.82 |
| O144 | 0.75 | 0.334(3) | 0.712(3) | 1.007(3) | 0.093(18) | C12 | 1 | 0.4975(18) | 0.179(2) | 1.1386(19) | 0.017(8) | 3.87 |
| O145 | 0.5 | 1.151(3) | 0.901(4) | 0.870(3) | 0.060(19) | C13 | 1 | 0.5052(16) | −0.093(2) | 1.1361(18) | 0.012(8) | 4.16 |
| O146 | 1 | 0.8277(15) | −0.1926(19) | 1.2113(17) | 0.047(9) | C14 | 1 | 1.009(2) | −0.179(3) | 1.479(3) | 0.048(15) | 3.94 |
| O147 | 1 | 0.824(2) | 0.807(3) | 0.953(2) | 0.116(16) | C15 | 1 | 0.4924(19) | 0.676(2) | 0.972(2) | 0.023(9) | 4.11 |
| O148 | 0.75 | 0.313(2) | −0.420(3) | 1.501(3) | 0.089(17) | C16 | 1 | 0.8840(19) | 0.376(2) | 1.744(2) | 0.030(10) | 4.12 |
| O149 | 0.75 | 0.863(2) | 0.413(3) | 1.175(3) | 0.090(18) | C17 | 1 | 0.6177(16) | 0.125(2) | 1.2574(18) | 0.013(6) | 3.95 |
| O150 | 0.5 | 0.723(2) | 0.543(3) | 1.283(3) | 0.042(15) | C18 | 1 | 0.9902(16) | 0.444(2) | 1.8851(19) | 0.013(6) | 4.01 |
| O151 | 0.3 | 0.836(4) | 0.483(5) | 1.045(5) | 0.03(2) | C19 | 1 | 0.4929(16) | 0.410(2) | 0.9720(18) | 0.013(8) | 4.13 |
| O152 | 0.5 | 0.719(4) | 0.255(5) | 0.620(4) | 0.09(3) | C20 | 1 | 0.5100(15) | 0.058(2) | 1.3792(19) | 0.011(8) | 3.97 |
| O153 | 0.5 | 1.208(3) | −0.300(3) | 1.549(3) | 0.042(15) | C21 | 1 | 1.0236(18) | 0.091(2) | 1.475(2) | 0.028(10) | 3.98 |
| O154 | 0.5 | 1.227(2) | −0.164(3) | 1.601(3) | 0.029(12) | C22 | 1 | 1.1217(19) | 0.394(2) | 1.770(2) | 0.032(11) | 3.71 |
| O155 | 0.5 | 0.807(3) | 0.929(3) | 0.858(3) | 0.046(16) | C23 | 1 | 0.386(2) | 0.110(3) | 1.253(2) | 0.038(12) | 4.05 |
| O156 | 0.5 | 0.805(4) | 0.257(5) | 1.131(4) | 0.09(3) | C24 | 1 | 1.320(2) | −0.253(3) | 1.307(2) | 0.046(13) | 3.92 |
| O157 | 0.5 | 1.174(3) | 0.326(5) | 1.594(4) | 0.08(3) |  |  |  |  |  |  |  |
| O158 | 0.5 | 0.704(3) | −0.422(4) | 1.349(4) | 0.08(2) |  |  |  |  |  |  |  |
| O159 | 0.5 | 1.162(3) | 1.028(4) | 0.695(3) | 0.055(19) |  |  |  |  |  |  |  |
| O160 | 0.5 | 0.284(3) | 0.367(4) | 0.661(4) | 0.06(2) |  |  |  |  |  |  |  |
| O161 | 0.25 | 0.673(4) | 0.058(5) | 1.554(4) | 0.02(2) |  |  |  |  |  |  |  |
| O162 | 0.5 | 0.767(2) | 0.497(3) | 1.248(3) | 0.030(13) |  |  |  |  |  |  |  |
| O163 | 0.5 | 0.850(4) | 0.457(5) | 1.075(4) | 0.08(3) |  |  |  |  |  |  |  |
| O164 | 0.2 | 1.261(6) | 1.157(8) | 0.617(7) | 0.04(4) |  |  |  |  |  |  |  |
| O165 | 0.2 | 1.245(6) | 1.097(8) | 0.707(7) | 0.04(4) |  |  |  |  |  |  |  |
| O166 | 0.5 | 1.214(4) | 0.146(6) | 1.491(5) | 0.12(3) |  |  |  |  |  |  |  |
| O167 | 0.5 | 0.811(4) | 0.458(5) | 1.243(4) | 0.10(3) |  |  |  |  |  |  |  |
| O168 | 0.25 | 1.317(5) | 1.334(6) | 0.666(5) | 0.03(3) |  |  |  |  |  |  |  |
| O169 | 0.25 | 1.234(5) | 1.070(7) | 0.591(6) | 0.05(3) |  |  |  |  |  |  |  |
| O170 | 0.5 | 1.147(3) | 0.236(4) | 1.470(4) | 0.07(2) |  |  |  |  |  |  |  |
| O171 | 0.25 | 0.775(4) | 0.190(5) | 1.128(5) | 0.02(2) |  |  |  |  |  |  |  |

Bond-valence parameters for U6+–O, Ca2+–O, Mg2+–O, and C4+–O taken from Gagné & Hawthorne [49]. .

**Table S2.** Anisotropic atomic displacement parameters (Å2) for paddlewheelite. .

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Site | U11 | U22 | U33 | U12 | U13 | U23 |
| U1 | 0.0198(10) | 0.0115(8) | 0.0518(13) | 0.0035(8) | −0.0007(8) | 0.0015(7) |
| U2 | 0.0429(10) | 0.0041(7) | 0.0134(9) | 0.0004(6) | 0.0032(7) | −0.0009(7) |
| U3 | 0.0549(12) | 0.0049(8) | 0.0131(9) | 0.0000(7) | −0.0005(9) | 0.0022(8) |
| U4 | 0.0638(13) | 0.0056(8) | 0.0108(9) | −0.0007(7) | −0.0039(8) | 0.0051(7) |
| U5 | 0.0505(10) | 0.0028(7) | 0.0137(8) | −0.0007(6) | 0.0010(7) | 0.0008(7) |
| U6 | 0.0209(10) | 0.0130(9) | 0.0453(12) | −0.0012(8) | −0.0014(8) | 0.0007(7) |
| U7 | 0.0210(10) | 0.0190(9) | 0.0330(11) | −0.0009(8) | −0.0014(8) | −0.0026(7) |
| U8 | 0.0180(10) | 0.0099(8) | 0.0908(16) | 0.0081(9) | 0.0002(10) | 0.0002(7) |
| Cu1 | 0.029(3) | 0.002(2) | 0.013(3) | −0.0003(18) | 0.002(2) | 0.000(2) |
| Cu2 | 0.026(3) | 0.007(2) | 0.009(3) | 0.0000(19) | −0.002(2) | −0.0008(19) |
| Cu3 | 0.026(2) | 0.003(2) | 0.020(3) | −0.0011(19) | −0.001(2) | 0.0003(19) |
| Cu4 | 0.028(3) | 0.004(2) | 0.020(3) | 0.001(2) | −0.002(2) | −0.001(2) |
| Ca1 | 0.018(4) | 0.006(3) | 0.022(4) | −0.001(2) | 0.003(3) | 0.001(3) |
| Ca2 | 0.019(4) | 0.006(3) | 0.009(3) | −0.002(2) | −0.004(3) | 0.002(2) |
| Ca3 | 0.097(9) | 0.007(4) | 0.023(5) | −0.001(3) | −0.009(5) | −0.001(5) |
| Ca4 | 0.100(9) | 0.009(4) | 0.011(5) | −0.003(3) | 0.004(5) | 0.006(5) |
| Ca5 | 0.068(7) | 0.007(4) | 0.018(5) | 0.002(3) | 0.002(4) | −0.002(4) |
| Ca6 | 0.049(6) | 0.005(4) | 0.023(5) | −0.004(3) | 0.000(4) | −0.004(4) |
| Ca7 | 0.030(5) | 0.018(4) | 0.057(6) | −0.005(4) | 0.009(4) | 0.002(4) |
| Ca8 | 0.034(5) | 0.012(4) | 0.067(7) | 0.000(4) | −0.018(5) | 0.003(4) |
| Ca9 | 0.030(5) | 0.013(4) | 0.044(6) | −0.004(4) | −0.004(4) | −0.005(3) |
| Ca10 | 0.023(5) | 0.023(5) | 0.127(10) | 0.025(6) | 0.009(6) | −0.001(4) |
| Mg1 | 0.033(8) | 0.007(6) | 0.026(8) | −0.006(5) | 0.006(6) | 0.004(5) |
| Mg2 | 0.024(7) | 0.003(5) | 0.020(7) | 0.000(5) | 0.002(5) | 0.005(5) |

**Table S3.** Selected bond distances (in Å) for paddlewheelite. .

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| U1−O113  U1−O8  U1−O63  U1−O35  U1−O19  U1−O12  U1−O75  U1−O33  <U1−OUr>  <U1−OEq>  U2−O123  U2−O41  U2−O3  U2−O66  U2−O9  U2−O83  U2−O27  U2−O10  <U2−OUr>  <U2−OEq>  U3−O18  U3−O20  U3−O17  U3−O15  U3−O68  U3−O99  U3−O78  U3−O52  <U3−OUr>  <U3−OEq>  U4−O96  U4−O6  U4−O86  U4−O76  U4−O55  U4−O37  U4−O62  U4−O108  <U4−OUr>  <U4−OEq>  U5−O85  U5−O81  U5−O13  U5−O42  U5−O70  U5−O7  U5−O32  U5−O28  <U5−OUr>  <U5−OEq> | 1.78(3)  1.85(4)  2.44(3)  2.41(3)  2.40(3)  2.45(3)  2.38(3)  2.43(3)  1.82  2.42  1.74(3)  1.76(3)  2.44(3)  2.41(3)  2.43(3)  2.37(3)  2.40(3)  2.47(3)  1.75  2.42  1.75(4)  1.75(3)  2.45(3)  2.40(3)  2.41(3)  2.46(3)  2.48(3)  2.46(3)  1.75  2.44  1.78(3)  1.80(4)  2.46(3)  2.42(3)  2.44(3)  2.41(3)  2.47(3)  2.45(3)  1.79  2.44  1.73(3)  1.77(3)  2.48(3)  2.41(3)  2.43(3)  2.41(3)  2.41(3)  2.41(3)  1.75  2.43 | U6−O146  U6−O112  U6−O64  U6−O71  U6−O67  U6−O44  U6−O46  U6−O50  <U6−OUr>  <U6−OEq>  U7−O21  U7−O14  U7−O31  U7−O25  U7−O39  U7−O53  U7−O74  U7−O118  <U7−OUr>  <U7−OEq>  U8−O82  U8−O1  U8−O87  U8−O54  U8−O94  U8−O121  U8−O49  U8−O58  <U8−OUr>  <U8−OEq>  Mg1−O117  Mg1−O40  Mg1−O80  Mg1−O56  Mg1−O29  Mg1−O69  <Mg1−O>  Mg2−O26  Mg2−O45  Mg2−O93  Mg2−O61  Mg2−O105  Mg2−O43  <Mg2−O>  Cu1−O34  Cu1−O95  Cu1−O72  Cu1−O30  Cu1−O36  <Cu1−O> | 1.77(4)  1.80(4)  2.34(3)  2.44(3)  2.48(3)  2.42(3)  2.46(3)  2.45(3)  1.79  2.43  1.73(4)  1.77(3)  2.41(3)  2.42(3)  2.47(3)  2.41(3)  2.43(3)  2.44(3)  1.75  2.43  1.62(4)  1.79(4)  2.43(4)  2.42(3)  2.42(3)  2.46(3)  2.43(3)  2.44(3)  1.71  2.43  2.03(4)  2.07(4)  2.06(3)  2.10(3)  2.08(3)  2.10(4)  2.07  2.11(3)  2.03(3)  2.07(4)  2.11(3)  2.10(3)  2.05(3)  2.08  1.96(3)  1.98(3)  1.97(3)  1.92(3)  2.19(3)  2.00 | Cu2−O92  Cu2−O11  Cu2−O65  Cu2−O57  Cu2−O47  <Cu2−O>  Cu3−O4  Cu3−O24  Cu3−O77  Cu3−O38  Cu3−O16  <Cu3−O>  Cu4−O5  Cu4−O60  Cu4−O02  Cu4−O23  Cu4−O22  <Cu4−O>  Ca1−O17  Ca1−O49  Ca1−O42  Ca1−O58  Ca1−O32  Ca1−O35  Ca1−O52  Ca1−O63  <Ca1−O>  Ca2−O46  Ca2−O50  Ca2−O9  Ca2−O62  Ca2−O55  Ca2−O31  Ca2−O27  Ca2−O25  <Ca2−O>  Ca3−O109  Ca3−O37  Ca3−O108  Ca3−O57  Ca3−O98  Ca3−O10  Ca3−O126  <Ca3−O> | 1.97(3)  1.96(3)  1.91(3)  1.98(3)  2.19(3)  2.00  1.98(3)  1.94(3)  1.93(3)  2.01(3)  2.22(3)  2.02  1.95(3)  1.98(3)  1.99(3)  1.96(3)  2.24(3)  2.02  2.35(3)  2.44(3)  2.35(3)  2.35(3)  2.47(4)  2.39(3)  2.47(4)  2.37(3)  2.40  2.41(4)  2.41(3)  2.44(3)  2.46(4)  2.32(4)  2.36(4)  2.37(3)  2.42(3)  2.40  2.38(4)  2.34(3)  2.42(3)  2.41(3)  2.38(3)  2.47(3)  2.33(5)  2.39 |
| Ca4−O111  Ca4−O3  Ca4−O66  Ca4−O142  Ca4−O86  Ca4−O4  Ca4−O122  <Ca4−O>  Ca5−O100  Ca5−O79  Ca5−O5  Ca5−O78  Ca5−O90  Ca5−O136  Ca5−O7  Ca5−O28  <Ca5−O>  Ca6−O68  Ca6−O101  Ca6−O99  Ca6−O72  Ca6−O13  Ca6−O88  Ca6−O48  <Ca6−O>  Ca7−O64  Ca7−O114  Ca7−O115  Ca7−O138  Ca7−O73  Ca7−O67  Ca7−O156  Ca7−O140  <Ca7−O>  Ca8−O159  Ca8−O150  Ca8−O134  Ca8−O19  Ca8−O163  Ca8−O168  Ca8−O127  Ca8−O75  Ca8−O103  Ca8−O120  <Ca8−O> | 2.31(4)  2.36(3)  2.36(3)  2.38(4)  2.49(3)  2.41(3)  2.45(4)  2.39  2.48(3)  2.41(3)  2.48(3)  2.46(4)  2.43(3)  2.55(3)  2.32(4)  2.41(4)  2.44  2.35(3)  2.40(5)  2.38(3)  2.42(3)  2.46(3)  2.38(3)  2.39(4)  2.40  2.41(3)  2.40(4)  2.32(5)  2.52(4)  2.43(4)  2.39(3)  2.39(6)  2.42(8)  2.41  2.48(7)  2.36(6)  2.63(7)  2.39(3)  2.39(6)  2.60(8)  2.39(4)  2.45(3)  2.45(4)  2.36(5)  2.45 | Ca9−O39  Ca9−O139  Ca9−O74  Ca9−O133  Ca9−O125  Ca9−O51  Ca9−O104  <Ca9−O>  Ca10−O107  Ca10−O132  Ca10−O84  Ca10−O54  Ca10−O128  Ca10−O131  Ca10−O121  <Ca10−O>  C1−O58  C1−O95  C1−O121  <C1−O>  C2−O54  C2−O87  C2−O91  <C2−O>  C3−O46  C3−O67  C3−O92  <C3−O>  C4−O108  C4−O62  C4−O65  <C4−O>  C5−O11  C5−O31  C5−O39  <C5−O>  C6−O43  C6−O64  C6−O71  <C6−O>  C7−O19  C7−O30  C7−O63  <C7−O> | 2.33(3)  2.47(4)  2.36(4)  2.35(4)  2.46(4)  2.41(3)  2.45(3)  2.40  2.45(4)  2.40(4)  2.42(3)  2.42(3)  2.39(4)  2.49(4)  2.39(3)  2.42  1.27(6)  1.32(6)  1.29(6)  1.29  1.27(7)  1.40(7)  1.33(8)  1.33  1.31(6)  1.23(6)  1.28(6)  1.27  1.30(5)  1.31(5)  1.26(5)  1.29  1.29(5)  1.32(5)  1.26(5)  1.29  1.21(5)  1.40(5)  1.31(5)  1.31  1.28(5)  1.37(5)  1.31(5)  1.32 | C8−O34  C8−O52  C8−O99  <C8−O>  C9−O4  C9−O55  C9−O86  <C9−O>  C10−O33  C10−O75  C10−O117  <C10−O>  C11−O83  C11−O66  C11−O16  <C11−O>  C12−O5  C12−O17  C12−O78  <C12−O>  C13−O22  C13−O28  C13−O70  <C13−O>  C14−O10  C14−O27  C14−O57  <C14−O>  C15−O13  C15−O72  C15−O42  <C15−O>  C16−O50  C16−O44  C16−O77  <C16−O>  C17−O2  C17−O12  C17−O35  <C17−O>  C18−O9  C18−O3  C18−O38  <C18−O> | 1.31(5)  1.29(5)  1.21(5)  1.27  1.30(5)  1.34(5)  1.21(5)  1.28  1.31(5)  1.23(5)  1.26(6)  1.27  1.29(5)  1.32(5)  1.28(5)  1.30  1.28(5)  1.23(5)  1.31(5)  1.30  1.22(5)  1.26(5)  1.33(5)  1.27  1.25(7)  1.31(7)  1.31(6)  1.29  1.34(5)  1.22(5)  1.29(5)  1.28  1.36(5)  1.26(5)  1.21(5)  1.28  1.28(5)  1.34(5)  1.25(5)  1.29  1.32(5)  1.29(5)  1.24(5)  1.28 |
| C19−O68  C19−O15  C19−O36  <C19−O>  C20−O7  C20−O23  C20−O32  <C20−O> | 1.28(5)  1.33(5)  1.21(5)  1.27  1.37(5)  1.23(5)  1.27(5)  1.29 | C21−O47  C21−O76  C21−O37  <C21−O>  C22−O24  C22−O25  C22−O53  <C22−O> | 1.20(5)  1.33(5)  1.34(5)  1.29  1.32(5)  1.31(5)  1.31(5)  1.31 | C23−O49  C23−O60  C23−O94  <C23−O>  C24−O74  C24−O89  C24−O118  <C23−O> | 1.28(6)  1.24(6)  1.32(6)  1.28  1.35(6)  1.24(6)  1.29(6)  1.29 |