**Supplementary Materials**

**Tab. 1S. Suppl.** Fractional site coordinates (*xyz*), site multiplicities (*Q*), equivalent displacement parameters (*U*eq, Å2) and site occupancy factor for crystals Ca9Y(VO4)7 (**1**), Ca9Y(VO4)7:Li+ (**2**) and Ca9Y(VO4)7:Mg2+ (**3**).

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Atom/Sample** | | ***x*** | ***y*** | ***z*** | ***Q*** | ***U*eq, Å2** | **s. o. f.** |
| *M*1 | 1 | 0.7243(1) | 0.8605(1) | 0.4258(1) | 18 | 0.0103(3) | Ca2+0.87(2)Y3+0.13(2) |
| 2 | 0.7242(1) | 0.8605(1) | 0.4258(1) | 18 | 0.0103(3) | Ca2+0.87(2)Y3+0.13(2) |
| 3 | 0.7250(1) | 0.8610(1) | 0.4252(3) | 18 | 0.0099(4) | Ca2+0.92(2)Y3+0.08(2) |
| *M*2 | 1 | 0.6132(1) | 0.8228(1) | 0.2288(1) | 18 | 0.0115(3) | Ca2+0.83(2)Y3+0.17(2) |
| 2 | 0.6131(1) | 0.8226(1) | 0.2288(1) | 18 | 0.0108(3) | Ca2+0.83(2)Y3+0.17(2) |
| 3 | 0.6135(1) | 0.8235(1) | 0.22798(3) | 18 | 0.0110(4) | Ca2+0.89(1)Y3+0.11(1) |
| *M*3 | 1 | 0.1247(1) | 0.2692(1) | 0.3198(1) | 18 | 0.0186(4) | Ca2+ |
| 2 | 0.1247(1) | 0.2692(1) | 0.3198(1) | 18 | 0.0180(4) | Ca2+ |
| 3 | 0.1243(1) | 0.2694(2) | 0.31904(4) | 18 | 0.0199(5) | Ca2+ |
| *M*5 | 1 | 0 | 0 | -0.0052(1) | 6 | 0.0242(3) | Ca2+0.89(2)Y3+0.11(2) |
| 2 | 0 | 0 | -0.0051(1) | 6 | 0.0229(4) | Ca2+0.91(2)Y3+0.09(2) |
| 3 | 0 | 0 | -0.0062(6) | 6 | 0.0368(5) | Ca2+0.41(2)Y3+0.44(2)Mg2+0.15(2) |
| V1 | 1 | 0 | 0 | 0.2626(1) | 6 | 0.0081(3) | V |
| 2 | 0 | 0 | 0.2626(1) | 6 | 0.0080(3) | V |
| 3 | 0 | 0 | 0.26153(4) | 6 | 0.0100(3) | V |
| V2 | 1 | 0.6835(1) | 0.8582(1) | 0.1292(1) | 18 | 0.0085(3) | V |
| 2 | 0.6834(1) | 0.8580(1) | 0.1292(1) | 18 | 0.0083(3) | V |
| 3 | 0.6846(1) | 0.8589(1) | 0.1286(3) | 18 | 0.0098(4) | V |
| V3 | 1 | 0.6542(1) | 0.8473(1) | 0.0273(1) | 18 | 0.0066(3) | V |
| 2 | 0.6538(1) | 0.8471(1) | 0.0272(1) | 18 | 0.0060(3) | V |
| 3 | 0.6535(1) | 0.8480(1) | 0.0266(3) | 18 | 0.0075(3) | V |
| O11 | 1 | 0 | 0 | 0.3077(2) | 6 | 0.0210(2) | O |
| 2 | 0 | 0 | 0.3080(2) | 6 | 0.0190(2) | O |
| 3 | 0 | 0 | 0.3066(2) | 6 | 0.0221(2) | O |
| O12 | 1 | -0.1571(4) | -0.0102(5) | 0.2511(2) | 18 | 0.0161(1) | O |
| 2 | -0.1575(4) | -0.0105(5) | 0.2511(2) | 18 | 0.0168(2) | O |
| 3 | -0.1573(5) | -0.0099(6) | 0.2500(2) | 18 | 0.0190(2) | O |
| O21 | 1 | 0.7054(8) | 0.8998(8) | 0.1722(2) | 18 | 0.042(3) | O |
| 2 | 0.7032(9) | 0.8986(8) | 0.1723(2) | 18 | 0.043(4) | O |
| 3 | 0.7065(9) | 0.9014(9) | 0.1717(2) | 18 | 0.046(4) | O |
| O22 | 1 | 0.7671(5) | 0.7679(5) | 0.1167(2) | 18 | 0.0196(2) | O |
| 2 | 0.7667(6) | 0.7683(6) | 0.1167(2) | 18 | 0.0180(2) | O |
| 3 | 0.7678(6) | 0.7690(6) | 0.1162(1) | 18 | 0.020(2) | O |
| O23 | 1 | 0.7240(4) | 1.0148(4) | 0.1079(2) | 18 | 0.0104(1) | O |
| 2 | 0.7243(4) | 1.0145(4) | 0.1078(2) | 18 | 0.0107(1) | O |
| 3 | 0.7239(5) | 1.0147(5) | 0.1068(1) | 18 | 0.013(2) | O |
| O24 | 1 | 0.5055(4) | 0.7500(5) | 0.1195(2) | 18 | 0.0222(2) | O |
| 2 | 0.5065(5) | 0.7507(6) | 0.1195(2) | 18 | 0.0231(2) | O |
| 3 | 0.5070(5) | 0.7507(6) | 0.1199(2) | 18 | 0.023(2) | O |
| O31 | 1 | 0.5915(5) | 0.9566(5) | 0.0393(2) | 18 | 0.0188(2) | O |
| 2 | 0.5926(5) | 0.9580(5) | 0.0394(2) | 18 | 0.0167(2) | O |
| 3 | 0.5931(5) | 0.9594(6) | 0.0384(1) | 18 | 0.019(2) | O |
| O32 | 1 | 0.5726(6) | 0.6846(5) | 0.0461(2) | 18 | 0.0277(2) | O |
| 2 | 0.5731(7) | 0.6842(6) | 0.0462(2) | 18 | 0.028(2) | O |
| 3 | 0.5706(7) | 0.6850(6) | 0.0458(2) | 18 | 0.032(2) | O |
| O33 | 1 | 0.8295(4) | 0.9278(5) | 0.0396(2) | 18 | 0.0161(1) | O |
| 2 | 0.8304(4) | 0.9280(5) | 0.0393(2) | 18 | 0.0136(2) | O |
| 3 | 0.8291(5) | 0.9269(5) | 0.0391(2) | 18 | 0.015(2) | O |
| O34 | 1 | 0.6290(5) | 0.8218(5) | -0.0162(2) | 18 | 0.0206(2) | O |
| 2 | 0.6294(6) | 0.8222(5) | -0.0165(2) | 18 | 0.0203(2) | O |
| 3 | 0.6285(6) | 0.8218(6) | -0.0170(1) | 18 | 0.021(2) | O |

Note: *U*eq is defined as one third of the trace of the orthogonalized *Uij* tensor.

**Tab. 2S. Suppl**. Anisotropic atomic displacement parameters (*Uij*, Å2) for crystals Ca9Y(VO4)7 (**1**), Ca9Y(VO4)7:Li+ (**2**) and Ca9Y(VO4)7:Mg2+ (**3**).

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Site** | **Sample** | ***U*11** | ***U*22** | ***U*33** | ***U*12** | ***U*13** | ***U*23** |
| *M*1 | 1 | 0.0109(4) | 0.0111(4) | 0.0097(3) | 0.0061(3) | -0.0007(3) | -0.0022(3) |
| 2 | 0.0102(5) | 0.0113(5) | 0.0087(4) | 0.0058(4) | -0.0002(4) | -0.0016(4) |
| 3 | 0.0108(4) | 0.0109(4) | 0.0100(3) | 0.0060(4) | -0.0004(3) | -0.0019(3) |
| *M*2 | 1 | 0.0118(4) | 0.0109(4) | 0.0110(3) | 0.0051(3) | -0.0028(3) | -0.0009(3) |
| 2 | 0.0120(5) | 0.0104(5) | 0.0090(4) | 0.0042(4) | -0.0035(4) | -0.0011(3) |
| 3 | 0.0112(4) | 0.0108(4) | 0.0093(3) | 0.0048(3) | -0.0028(3) | -0.0006(3) |
| *M*3 | 1 | 0.0148(4) | 0.0240(5) | 0.0157(4) | 0.0088(4) | -0.0024(4) | 0.0083(4) |
| 2 | 0.0146(5) | 0.0259(6) | 0.0179(5) | 0.0092(5) | -0.0012(5) | 0.0104(5) |
| 3 | 0.0132(5) | 0.0238(6) | 0.0152(4) | 0.0079(5) | -0.0025(4) | 0.0083(4) |
| *M*5 | 1 | 0.0342(5) | 0.0342(5) | 0.0043(5) | 0.0171(2) | 0 | 0 |
| 2 | 0.0490(6) | 0.0490(6) | 0.0126(6) | 0.0245(3) | 0 | 0 |
| 3 | 0.0328(5) | 0.0328(5) | 0.0030(4) | 0.0164(3) | 0 | 0 |
| V1 | 1 | 0.0072(3) | 0.0072(3) | 0.0098(5) | 0.0036(2) | 0 | 0 |
| 2 | 0.0097(4) | 0.0097(4) | 0.0106(6) | 0.0048(2) | 0 | 0 |
| 3 | 0.0078(3) | 0.0078(3) | 0.0085(5) | 0.0039(2) | 0 | 0 |
| V2 | 1 | 0.0108(4) | 0.0099(4) | 0.0077(4) | 0.0074(3) | 0.0031(3) | 0.0020(3) |
| 2 | 0.0121(4) | 0.0119(5) | 0.0082(5) | 0.0081(4) | 0.0033(4) | 0.0022(4) |
| 3 | 0.0104(4) | 0.0100(4) | 0.0073(4) | 0.0071(3) | 0.0032(3) | 0.0022(3) |
| V3 | 1 | 0.0052(3) | 0.0081(3) | 0.0052(3) | 0.0024(3) | 0.0001(3) | 0.0004(3) |
| 2 | 0.0071(4) | 0.0094(4) | 0.0053(4) | 0.0037(4) | 0.0006(3) | 0.0009(3) |
| 3 | 0.0054(3) | 0.0067(3) | 0.0048(3) | 0.0022(3) | -0.0001(3) | 0.0006(3) |
| O11 | 1 | 0.030(2) | 0.030(2) | 0.002(2) | 0.015(1) | 0 | 0 |
| 2 | 0.031(3) | 0.031(3) | 0.005(3) | 0.015(1) | 0 | 0 |
| 3 | 0.025(2) | 0.025(2) | 0.007(2) | 0.013(1) | 0 | 0 |
| O12 | 1 | 0.013(2) | 0.021(2) | 0.018(2) | 0.012(2) | -0.005(1) | -0.009(2) |
| 2 | 0.012(2) | 0.021(2) | 0.023(3) | 0.009(2) | -0.007(2) | -0.010(2) |
| 3 | 0.012(2) | 0.018(2) | 0.022(2) | 0.008(2) | -0.004(2) | -0.008(2) |
| O21 | 1 | 0.074(4) | 0.069(4) | 0.013(2) | 0.058(4) | 0.005(2) | 0.000(2) |
| 2 | 0.088(6) | 0.080(5) | 0.011(2) | 0.071(5) | 0.003(3) | 0.002(3) |
| 3 | 0.081(5) | 0.073(5) | 0.007(2) | 0.063(4) | 0.006(2) | 0.004(2) |
| O22 | 1 | 0.025(2) | 0.028(2) | 0.020(2) | 0.024(2) | 0.006(2) | 0.005(2) |
| 2 | 0.027(3) | 0.025(3) | 0.019(2) | 0.021(2) | 0.009(2) | 0.005(2) |
| 3 | 0.027(2) | 0.024(2) | 0.014(2) | 0.021(2) | 0.005(2) | 0.002(2) |
| O23 | 1 | 0.005(2) | 0.009(1) | 0.015(2) | 0.001(1) | 0.001(1) | 0.003(1) |
| 2 | 0.012(2) | 0.011(2) | 0.015(2) | 0.005(2) | 0.002(2) | 0.001(2) |
| 3 | 0.010(2) | 0.008(2) | 0.013(2) | 0.003(2) | 0.001(2) | 0.002(2) |
| O24 | 1 | 0.007(2) | 0.011(2) | 0.046(3) | 0.003(2) | 0.0057(2) | 0.001(2) |
| 2 | 0.014(2) | 0.011(2) | 0.040(3) | 0.003(2) | 0.006(2) | 0.002(2) |
| 3 | 0.010(2) | 0.011(2) | 0.048(3) | 0.004(2) | 0.007(2) | 0.001(2) |
| O31 | 1 | 0.026(2) | 0.033(2) | 0.011(2) | 0.024(2) | -0.005(2) | -0.003(2) |
| 2 | 0.029(3) | 0.033(3) | 0.007(2) | 0.025(2) | -0.003(2) | -0.007(2) |
| 3 | 0.023(2) | 0.026(2) | 0.013(2) | 0.021(2) | -0.003(2) | -0.005(2) |
| O32 | 1 | 0.036(3) | 0.020(2) | 0.021(2) | 0.009(2) | 0.009(2) | 0.012(2) |
| 2 | 0.038(3) | 0.024(3) | 0.024(3) | 0.007(3) | 0.011(2) | 0.016(2) |
| 3 | 0.034(3) | 0.018(2) | 0.023(2) | 0.006(2) | 0.011(2) | 0.012(2) |
| O33 | 1 | 0.013(2) | 0.018(2) | 0.021(2) | 0.010(2) | -0.002(2) | -0.007(2) |
| 2 | 0.008(2) | 0.010(2) | 0.025(2) | 0.003(2) | -0.003(2) | -0.006(2) |
| 3 | 0.007(2) | 0.014(2) | 0.020(2) | 0.005(2) | -0.004(1) | -0.006(2) |
| O34 | 1 | 0.035(2) | 0.028(2) | 0.008(2) | 0.023(2) | -0.008(2) | -0.001(2) |
| 2 | 0.037(3) | 0.026(3) | 0.007(2) | 0.020(2) | 0.001(2) | -0.001(2) |
| 3 | 0.037(3) | 0.025(2) | 0.0061(2) | 0.021(2) | -0.001(2) | -0.001(2) |