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Supporting information for article:

Extraordinary structural complexity of ilmajokite: a multilevel hierarchical framework structure of natural origin

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Table S1. EMPA analyses if ilmajokite (normalized on the basis of 109 O pfu)

| point | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | average | average* | average** |
|--------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|----------|-----------|
| SiO ₂ | 48.45 | 50.00 | 50.73 | 49.01 | 51.32 | 52.05 | 49.72 | 52.38 | 52.00 | 52.14 | 49.47 | 50.66 | 49.53 | 49.53 |
| Al ₂ O ₃ | 0.02 | 0.04 | 0.03 | 0.06 | 0.05 | 0.04 | 0.02 | 0.01 | 0.02 | 0.04 | 0.00 | 0.03 | 0.03 | 0.03 |
| TiO ₂ | 21.07 | 20.84 | 22.05 | 20.60 | 21.27 | 21.69 | 21.68 | 22.49 | 22.67 | 21.80 | 20.03 | 21.47 | 20.92 | 20.92 |
| FeO | 0.01 | 0.01 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | 0.03 | 0.03 | 0.00 | 0.02 | 0.01 | 0.01 |
| MnO | 0.02 | 0.00 | 0.02 | 0.00 | 0.04 | 0.02 | 0.00 | 0.00 | 0.00 | 0.03 | 0.01 | 0.01 | 0.01 | 0.01 |
| MgO | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| CaO | 0.10 | 0.08 | 0.10 | 0.09 | 0.08 | 0.06 | 0.07 | 0.10 | 0.10 | 0.10 | 0.12 | 0.09 | 0.10 | 0.10 |
| BaO | 2.98 | 2.89 | 2.75 | 2.52 | 3.22 | 3.18 | 3.15 | 3.41 | 3.30 | 3.00 | 2.89 | 3.03 | 2.80 | 2.80 |
| Na ₂ O ⁻ | 7.29 | 5.18 | 4.93 | 6.71 | 2.66 | 3.27 | 3.33 | 1.37 | 1.37 | 0.68 | 8.22 | 4.09 | 6.47 | 6.47 |
| K ₂ O | 1.00 | 1.26 | 1.12 | 1.03 | 1.21 | 1.07 | 1.09 | 0.97 | 0.89 | 0.78 | 1.20 | 1.06 | 1.12 | 1.12 |
| Nb ₂ O ₅ | 0.00 | 0.07 | 0.08 | 0.00 | 0.05 | 0.07 | 0.11 | 0.00 | 0.00 | 0.42 | 0.00 | 0.08 | 0.03 | 0.03 |
| Ta ₂ O ₅ | 0.00 | 0.19 | 0.37 | 0.20 | 0.00 | 0.05 | 0.07 | 0.05 | 0.17 | 0.19 | 0.00 | 0.13 | 0.15 | 0.15 |
| La ₂ O ₃ | 1.89 | 2.29 | 2.02 | 2.17 | 1.76 | 2.55 | 1.83 | 2.34 | 2.08 | 2.41 | 2.08 | 2.13 | 2.09 | 2.09 |
| Ce ₂ O ₃ | 3.36 | 3.36 | 3.95 | 3.42 | 3.87 | 3.64 | 3.23 | 3.74 | 3.58 | 3.28 | 3.69 | 3.56 | 3.56 | 3.56 |
| Pr ₂ O ₃ | 0.05 | 0.55 | 0.39 | 0.52 | 0.54 | 0.00 | 0.20 | 0.33 | 0.36 | 0.41 | 0.22 | 0.32 | 0.35 | 0.35 |
| Nd ₂ O ₃ | 0.86 | 1.11 | 1.16 | 0.90 | 0.69 | 0.87 | 0.62 | 0.74 | 1.15 | 0.63 | 0.88 | 0.87 | 0.98 | 0.98 |
| Sm ₂ O ₃ | 0.03 | 0.19 | 0.30 | 0.03 | 0.16 | 0.00 | 0.00 | 0.25 | 0.00 | 0.19 | 0.01 | 0.10 | 0.11 | 0.11 |
| Dy ₂ O ₃ | 0.28 | 0.00 | 0.00 | 0.00 | 0.00 | 0.51 | 0.01 | 0.03 | 0.11 | 0.00 | 0.00 | 0.09 | 0.06 | 0.06 |
| ZrO ₂ | 0.00 | 0.00 | 0.00 | 0.04 | 0.03 | 0.03 | 0.03 | 0.00 | 0.02 | 0.00 | 0.06 | 0.02 | 0.02 | 0.02 |
| ThO ₂ | 0.56 | 0.41 | 0.49 | 0.48 | 0.48 | 0.39 | 0.46 | 0.43 | 0.27 | 0.54 | 0.34 | 0.44 | 0.46 | 0.46 |
| Y ₂ O ₃ | 0.02 | 0.02 | 0.02 | 0.00 | 0.06 | 0.00 | 0.07 | 0.00 | 0.07 | 0.00 | 0.00 | 0.02 | 0.01 | 0.01 |
| F | 0.00 | 0.01 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | 0.03 | 0.03 | 0.00 | 0.02 | 0.01 | 0.01 |
| H ₂ O* | | | | | | | | | | | | | | 11.50 |
| TOTAL | 87.98 | 88.50 | 90.56 | 87.78 | 87.51 | 89.50 | 85.71 | 88.80 | 88.22 | 86.72 | 89.25 | 88.25 | 88.82 | 100.32 |
| O=F | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.01 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| TOTAL | 87.98 | 88.50 | 90.55 | 87.78 | 87.51 | 89.50 | 85.71 | 88.77 | 88.21 | 86.70 | 89.25 | 88.25 | 88.81 | 100.31 |
| Si | 37.338 | 38.093 | 37.765 | 37.703 | 38.938 | 38.742 | 38.418 | 38.975 | 38.861 | 39.357 | 37.686 | 38.350 | 37.718 | 37.718 |
| Al | 0.018 | 0.035 | 0.030 | 0.059 | 0.042 | 0.035 | 0.014 | 0.007 | 0.016 | 0.038 | 0.000 | 0.027 | 0.028 | 0.028 |
| Σ T | 37.356 | 38.128 | 37.795 | 37.762 | 38.980 | 38.777 | 38.432 | 38.981 | 38.877 | 39.395 | 37.686 | 38.377 | 37.746 | 37.746 |
| Ti | 12.212 | 11.941 | 12.346 | 11.917 | 12.136 | 12.140 | 12.601 | 12.585 | 12.742 | 12.377 | 11.475 | 12.224 | 11.979 | 11.979 |
| Nb | 0.000 | 0.023 | 0.026 | 0.000 | 0.018 | 0.023 | 0.039 | 0.000 | 0.000 | 0.142 | 0.002 | 0.027 | 0.010 | 0.010 |
| Sn ⁴⁺ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Ta | 0.000 | 0.058 | 0.113 | 0.062 | 0.000 | 0.016 | 0.021 | 0.014 | 0.050 | 0.059 | 0.000 | 0.039 | 0.047 | 0.047 |
| Fe ³⁺ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Fe ²⁺ | 0.003 | 0.008 | 0.015 | 0.000 | 0.000 | 0.000 | 0.000 | 0.044 | 0.018 | 0.022 | 0.000 | 0.010 | 0.005 | 0.005 |
| Mn ²⁺ | 0.015 | 0.000 | 0.013 | 0.000 | 0.026 | 0.011 | 0.000 | 0.000 | 0.000 | 0.017 | 0.009 | 0.008 | 0.007 | 0.007 |
| Mg | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 |
| Zr | 0.000 | 0.000 | 0.000 | 0.015 | 0.012 | 0.012 | 0.013 | 0.000 | 0.008 | 0.000 | 0.024 | 0.008 | 0.008 | 0.008 |
| Na | 10.900 | 7.658 | 7.114 | 10.007 | 3.916 | 4.719 | 4.996 | 1.970 | 1.986 | 0.995 | 12.141 | 6.007 | 9.549 | 9.549 |
| La | 0.537 | 0.642 | 0.555 | 0.616 | 0.492 | 0.701 | 0.522 | 0.642 | 0.573 | 0.671 | 0.583 | 0.594 | 0.587 | 0.587 |
| Ce ³⁺ | 0.948 | 0.937 | 1.076 | 0.964 | 1.074 | 0.991 | 0.915 | 1.019 | 0.979 | 0.907 | 1.030 | 0.986 | 0.992 | 0.992 |
| Pr | 0.013 | 0.153 | 0.105 | 0.146 | 0.148 | 0.000 | 0.055 | 0.089 | 0.098 | 0.112 | 0.062 | 0.089 | 0.096 | 0.096 |
| Nd | 0.238 | 0.301 | 0.309 | 0.248 | 0.187 | 0.231 | 0.171 | 0.198 | 0.306 | 0.170 | 0.240 | 0.236 | 0.268 | 0.268 |
| Sm | 0.007 | 0.049 | 0.077 | 0.007 | 0.043 | 0.000 | 0.000 | 0.065 | 0.000 | 0.048 | 0.002 | 0.027 | 0.029 | 0.029 |

| | | | | | | | | | | | | | | |
|----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| Dy | 0.069 | 0.000 | 0.000 | 0.000 | 0.000 | 0.123 | 0.003 | 0.008 | 0.026 | 0.000 | 0.000 | 0.021 | 0.014 | 0.014 |
| Ca | 0.082 | 0.066 | 0.079 | 0.076 | 0.063 | 0.048 | 0.061 | 0.080 | 0.076 | 0.077 | 0.097 | 0.073 | 0.080 | 0.080 |
| Th | 0.098 | 0.071 | 0.083 | 0.083 | 0.083 | 0.066 | 0.080 | 0.073 | 0.045 | 0.093 | 0.059 | 0.076 | 0.079 | 0.079 |
| K | 0.981 | 1.220 | 1.060 | 1.007 | 1.176 | 1.012 | 1.074 | 0.923 | 0.847 | 0.752 | 1.169 | 1.019 | 1.088 | 1.088 |
| Ba | 0.899 | 0.864 | 0.801 | 0.759 | 0.958 | 0.926 | 0.954 | 0.996 | 0.967 | 0.887 | 0.862 | 0.898 | 0.837 | 0.837 |
| Y | 0.009 | 0.008 | 0.006 | 0.000 | 0.025 | 0.000 | 0.031 | 0.000 | 0.029 | 0.000 | 0.000 | 0.010 | 0.005 | 0.005 |
| F | 0.000 | 0.031 | 0.055 | 0.000 | 0.000 | 0.000 | 0.000 | 0.166 | 0.068 | 0.081 | 0.000 | 0.041 | 0.018 | 0.018 |
| OH | | | | | | | | | | | | | | 58.463 |

* Average of analyses 1,2,3,4,11. ** Average of analyses 1,2,3,4,11 with calculated H₂O content to reach observed cation sums and normalized on the basis of 138.23 O pfu.

Table S2. Standards used:

| Standard | WDS line and analyzing crystal |
|---|--|
| Ba ₂ NaNb ₅ O ₁₅ | BaL α , LLIF; NbL α , LPET |
| MnNb ₂ Ta ₂ O ₉ | TaL α , LLIF |
| titanite | TiK α , LLIF |
| zircon | ZrL α , LPET |
| ThO ₂ | ThM α , LPET |
| diopside | SiK α , TAP; CaK α , LPET |
| andalusite | AlK α , TAP |
| LaPO ₄ | LaL α , LLIF |
| CePO ₄ | CeL α , LLIF |
| PrPO ₄ | PrL β , LLIF |
| NdPO ₄ | NdL β , LLIF |
| SmPO ₄ | SmL β , LLIF |
| DyPO ₄ | DyL β , LLIF |
| YPO ₄ | YL α , LPET |
| fayalite | FeK α , LLIF |
| spessartine | MnK α , LLIF |
| forsterite | MgK α , LTAP |
| orthoclase | KK α , LPET |
| albite | NaK α , TAP |
| pollucite | CsL α , LPET |
| F-bearing riebeckite | FK α , LTAP * |

*Overlap of BaL β on CeL α and CeM ζ on FK α were accounted for; elements Zn, Sr, Gd, and U were sought but not detected.

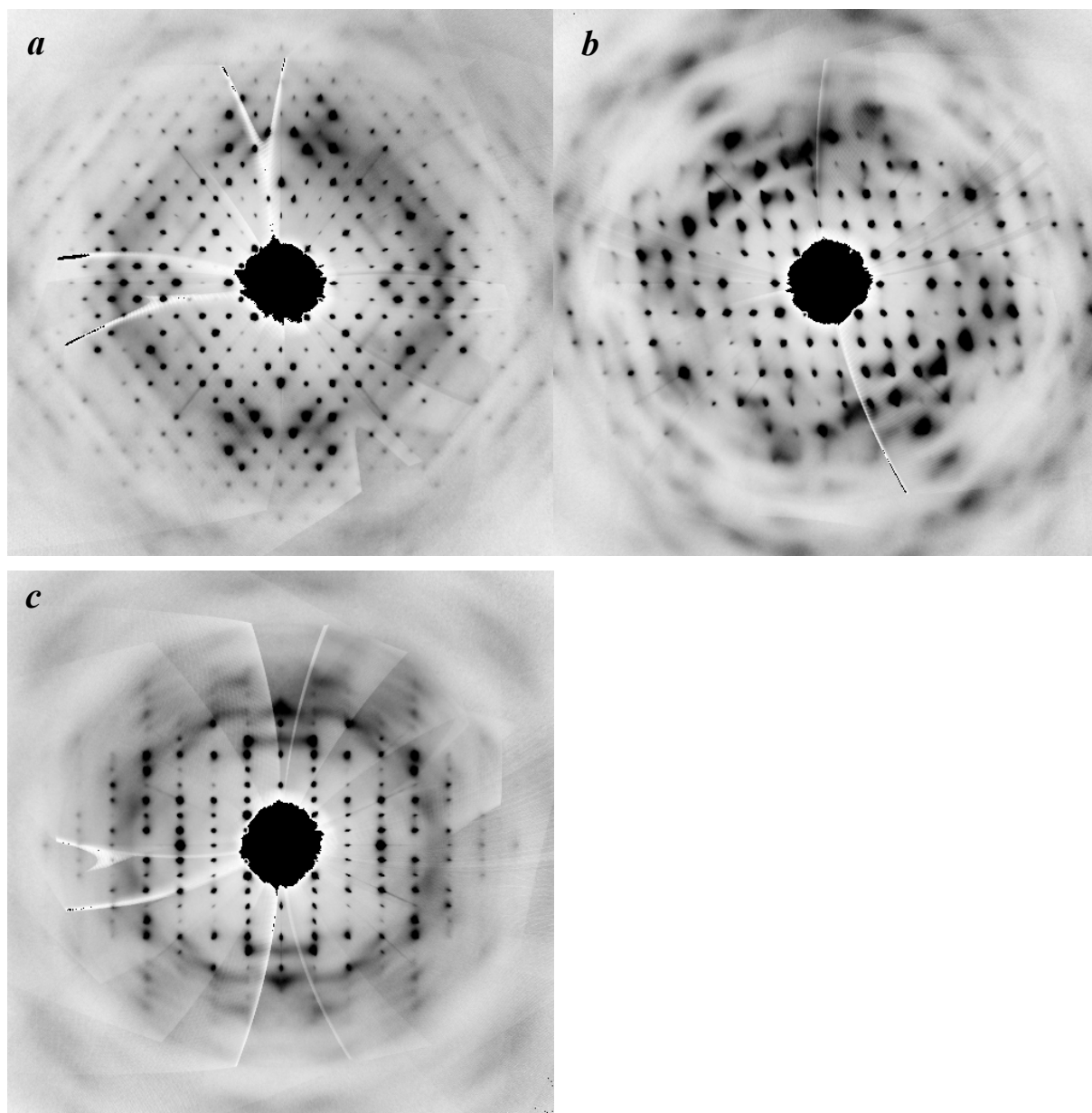


Figure S1 Unwrapped sections of the reciprocal space .a $hk0$, b $h0l$, c $0kl$ for crystal ILM02.

Note that the mosaicity starts at lower resolution along $[-101]$, the direction of the ribbons in the (010) layers.

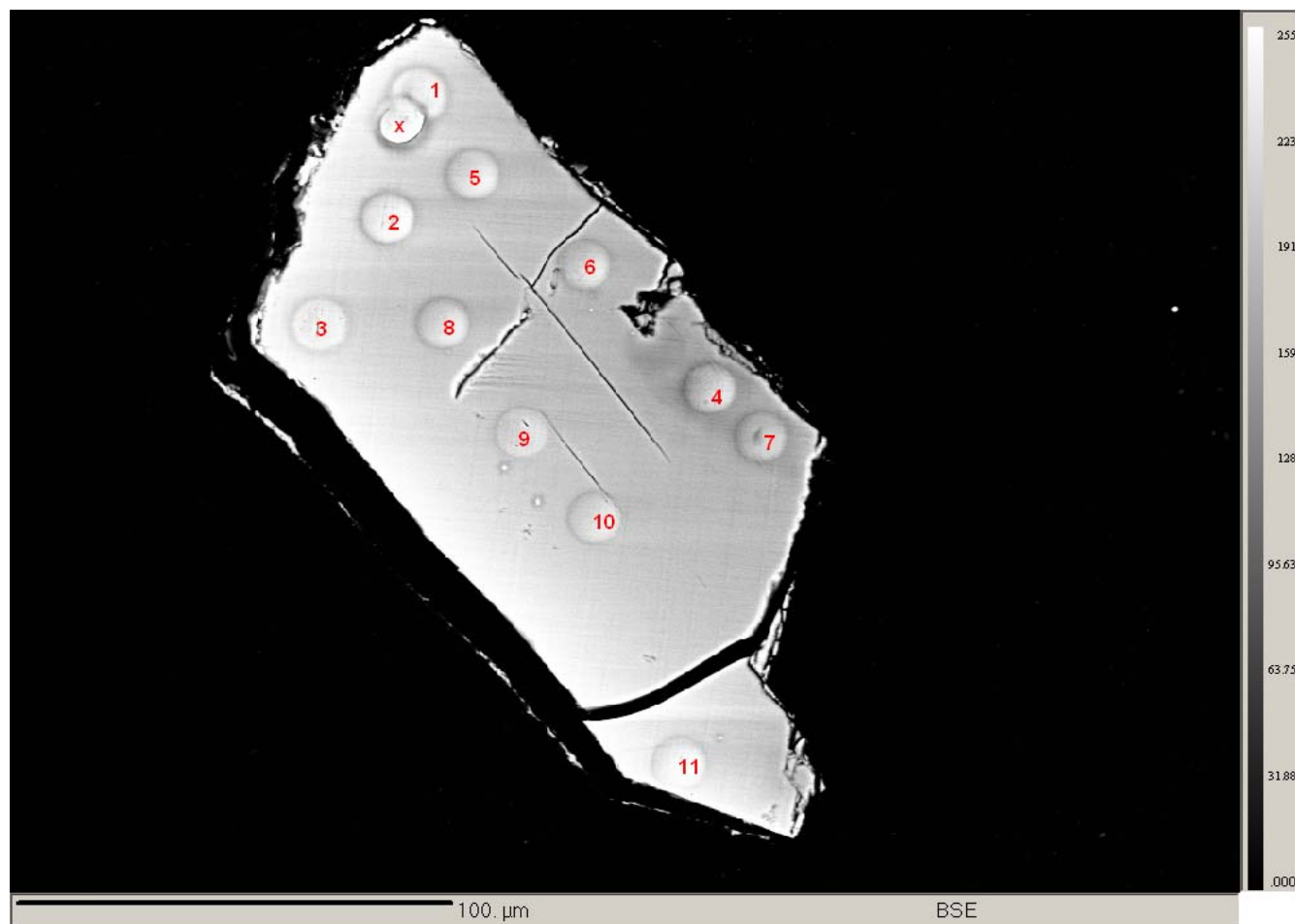


Figure S2. BSE image of the analyzed crystal. Numbers correspond to analyses in Table 3. X is a test spot to check beam sensitivity at 10nA and 15 µm Ø (i.e. counts vs. time test), no quantitative data acquired. The damage of the beam is evident.