Table S1. Crystal cell parameters *a* and *c*, *R*-factors, and average M-O distances *d* (M = Fe, Mn) in BaFe12-*x*Mn*x*O19, where *x* = 0, 2, 4, 6 (samples **1**, **2** ,**3**, **4**, respectively), annealed at 900, 1000, 1100, 1200 °C (samples’ second symbol **a**, **b**, **c**, **d**, respectively). Values of *a*, *c*, and *d* are in Å.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | *a* (Å) | *c* (Å) | *R*wp, *R*all | *d*(M1-O) | *d*(M2-O) | *d*(M3-O) | *d*(M4-O) | *d*(M5-O) |
| **1a** | 5.8950(1) | 23.2182(3) | 0.031, 0.019 | 2.013(5) | 1.914(9) | 1.887(6) | 2.023(6) | 2.032(4) |
| **1b** | 5.8949(1) | 23.2135(2) | 0.029, 0.019 | 2.020(5) | 1.916(7) | 1.883(5) | 2.020(5) | 2.032(3) |
| **1c** | 5.8941(1) | 23.2067(2) | 0.036, 0.015 | 2.008(4) | 1.920(6) | 1.888(4) | 2.020(4) | 2.031(3) |
| **1d** | 5.8951(1) | 23.2106(2) | 0.038, 0.017 | 2.014(4) | 1.920(6) | 1.887(4) | 2.020(4) | 2.032(3) |
| **2a** | 5.8965(1) | 23.1981(3) | 0.031, 0.016 | 2.016(5) | 1.921(8) | 1.913(6) | 2.016(6) | 2.024(3) |
| **2b** | 5.8972(1) | 23.1985(3) | 0.028, 0.023 | 2.008(5) | 1.909(9) | 1.914(6) | 2.025(6) | 2.024(4) |
| **2c** | 5.8965(1) | 23.1929(2) | 0.035, 0.015 | 2.003(4) | 1.922(6) | 1.914(4) | 2.015(4) | 2.027(3) |
| **2d** | 5.8987(1) | 23.1978(2) | 0.039, 0.016 | 2.004(4) | 1.922(6) | 1.920(4) | 2.013(4) | 2.025(3) |
| **3a** | 5.9006(1) | 23.1746(3) | 0.028, 0.016 | 2.010(5) | 1.928(7) | 1.936(5) | 2.014(5) | 2.018(4) |
| **3b** | 5.9009(1) | 23.1720(3) | 0.028, 0.022 | 2.011(5) | 1.941(8) | 1.939(6) | 2.009(6) | 2.016(4) |
| **3c** | 5.9020(1)  | 23.1707(2) | 0.030, 0.018 | 2.002(5) | 1.919(7) | 1.945(5) | 2.015(5) | 2.019(3) |
| **3d** | 5.9025(1) | 23.1743(2) | 0.042, 0.016 | 1.996(4) | 1.915(6) | 1.953(4) | 2.018(4) | 2.014(3) |
| **4a** | 5.9065(1) | 23.1439(3) | 0.027, 0.017 | 1.992(5) | 1.950(7) | 1.961(5) | 2.003(6) | 2.014(4) |
| **4b** | 5.9066(1) | 23.1420(3) | 0.028, 0.021 | 1.983(5) | 1.935(8) | 1.967(6) | 2.007(6) | 2.015(4) |
| **4c** | 5.9078(1) | 23.1426(3) | 0.029, 0.028 | 1.985(5) | 1.921(8) | 1.981(6) | 2.016(6) | 2.009(4) |
| **4d** | 5.9091(1) | 23.1494(2) | 0.042, 0.023 | 1.977(4) | 1.918(6) | 1.980(4) | 2.020(4) | 2.008(3) |

Table S2. Atomic parameters in the crystal structure of BaFe12O19 annealed at 1200 °C.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom | Occupancy | *x*/*a* | *y*/*a* | *z*/*c* | *U*iso (Å2) |
| Ba | 1 | 2/3 | 1/3 | 1/4 | 0.0065(2) |
| Fe1 | 1 | 0 | 0 | 0 | 0.0048(4) |
| Fe2 | 0.5 | 0 | 0 | 0.25869(14) | 0.0039(6) |
| Fe3 | 1 | 1/3 | 2/3 | 0.02733(6) | 0.0045(3) |
| Fe4 | 1 | 1/3 | 2/3 | 0.19032(5) | 0.0047(3) |
| Fe5 | 1 | 0.16853(9) | 0.33706(19) | 0.89168(3) | 0.0048(2) |
| O1 | 1 | 0 | 0 | 0.1492(2) | 0.0063(4) |
| O2 | 1 | 2/3 | 1/3 | 0.0540(2) | 0.0063(4) |
| O3 | 1 | 0.1799(5) | 0.3597(11) | 1/4 | 0.0063(4) |
| O4 | 1 | 0.1575(4) | 0.3150(8) | 0.05221(12) | 0.0063(4) |
| O5 | 1 | 0.5002(4) | 0.0003(8) | 0.14964(13) | 0.0063(4) |

Table S3. Atomic parameters in the crystal structure of BaFe6Mn6O19 annealed at 1200 °C.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom | Occupancy | *x*/*a* | *y*/*a* | *z*/*c* | *U*iso (Å2) |
| Ba | 1 | 2/3 | 1/3 | 1/4 | 0.0093(2) |
| M1 | 1 | 0 | 0 | 0 | 0.0095(5) |
| M2 | 0.5 | 0 | 0 | 0.25908(14) | 0.0022(7) |
| M3 | 1 | 1/3 | 2/3 | 0.02768(7) | 0.0103(3) |
| M4 | 1 | 1/3 | 2/3 | 0.19062(6) | 0.0069(3) |
| M5 | 1 | 0.16737(11) | 0.3347(2) | 0.89196(3) | 0.0082(2) |
| O1 | 1 | 0 | 0 | 0.1514(3) | 0.0154(5) |
| O2 | 1 | 2/3 | 1/3 | 0.0587(2) | 0.0154(5) |
| O3 | 1 | 0.1813(6) | 0.3626(12) | 1/4 | 0.0154(5) |
| O4 | 1 | 0.1499(4) | 0.2998(8) | 0.05387(14) | 0.0154(5) |
| O5 | 1 | 0.5012(4) | 0.0023(9) | 0.14962(16) | 0.0154(5) |

|  |  |  |
| --- | --- | --- |
| *x* = 0, *T*an = 900 °C | *x* = 0, *T*an = 1100 °C | *x* = 0, *T*an = 1200 °C |
| *x* = 2, *T*an = 900 °C | *x* = 2, *T*an = 1100 °C | *x* = 2, *T*an = 1200 °C |
| *x* = 4, *T*an = 900 °C | *x* = 4, *T*an = 1100 °C | *x* = 4, *T*an = 1200 °C |
| *x* = 6, *T*an = 900 °C | *x* = 6, *T*an = 1100 °C | *x* = 6, *T*an = 1200 °C |

Fig. S1. Scanning electron microscopy images of BaFe12-xMnxO19 samples annealed at *T*an.



Fig. S2. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 0, *T*an = 900 °C.



Fig. S3. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 0, *T*an = 1000 °C.



Fig. S4. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 0, *T*an = 1100 °C.



Fig. S5. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 0, *T*an = 1200 °C.



Fig. S6. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 2, *T*an = 900 °C.



Fig. S7. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 2, *T*an = 1000 °C.



Fig. S8. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 2, *T*an = 1100 °C.



Fig. S9. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 2, *T*an = 1200 °C.



Fig. S10. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 4, *T*an = 900 °C.



Fig. S11. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 4, *T*an = 1000 °C.



Fig. S12. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 4, *T*an = 1100 °C.



Fig. S13. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 4, *T*an = 1200 °C.



Fig. S14. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 6, *T*an = 900 °C.



Fig. S15. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 6, *T*an = 1000 °C.



Fig. S16. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 6, *T*an = 1100 °C.



Fig. S17. Observed (crosses), calculated (line), and difference (line underneath) XRD patterns of BaFe12-*x*Mn*x*O19, *x* = 6, *T*an = 1200 °C.