

## SUPPORTING INFORMATION

### **Polymorphs, phase transitions and stability in $\text{BaM}_2(\text{PO}_4)_2$ $\text{M} = \text{Mn, Fe, Co}$ systems**

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| Powder Data (T=293K)                                          |                                                           |
|---------------------------------------------------------------|-----------------------------------------------------------|
| Formula                                                       | $\alpha$ -BaFe <sub>2</sub> P <sub>2</sub> O <sub>8</sub> |
| Molar weight (g/mol)                                          | 438,968                                                   |
| Symmetry                                                      | Trigonal                                                  |
| Space group                                                   | P 3 <sub>1</sub> 2 1 (152)                                |
| Unit cell (Å) and angle (°)                                   | a = 5,114124(14)<br>c = 25,11130(8)                       |
| Volume (Å <sup>3</sup> )                                      | 568,777(3)                                                |
| Z                                                             | 3                                                         |
| Data collection                                               |                                                           |
| Equipment                                                     | Synchrotron (I11-DIAMOND)                                 |
| $\lambda$ (K $\alpha$ ; Å)                                    | 0,824899                                                  |
| Sample Holder                                                 | 0,5mm Glass Capillary                                     |
| density calc. (g/cm <sup>3</sup> )                            | 3,8448                                                    |
| Sample                                                        | Powder                                                    |
| Color                                                         | grey                                                      |
| $\theta$ (min-max) (°)                                        | 2,10800 - 92,11200                                        |
| $\mu$ (mm <sup>-1</sup> for $\lambda$ (K $\alpha$ =0,824899Å) | 13,884                                                    |
| R <sub>Bragg</sub> (%)                                        | 6,629                                                     |

*Table SIb. Atomic Positions & equivalent anisotropic thermal displacement for  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> structure.*

| Atom | Wick. | x           | y          | z           | Ueq (Å <sup>2</sup> ) |
|------|-------|-------------|------------|-------------|-----------------------|
| Ba1  | 3a    | 0,04080(15) | 0,000000   | 0,33333     | 0,00291(8)            |
| Fe1  | 6c    | 0.6849(6)   | 0.2596(5)  | 0.21819(7)  | 0.0274(6)             |
| P1   | 6c    | 0.6547(7)   | 0.3408(6)  | 0.08844(9)  | 0.0519(9)             |
| O1   | 6c    | 0.7176(11)  | 0.4602(10) | 0.14559(12) | 0.0550(14)            |
| O2   | 6c    | 0.8988(9)   | 0.5303(10) | 0.05088(18) | 0.0550(14)            |
| O3   | 6c    | 0.5843(11)  | 0.0073(7)  | 0.08565(18) | 0.0550(14)            |
| O4   | 6c    | 0.3471(8)   | 0.3197(11) | 0.07184(18) | 0.0550(14)            |

**(S2) Structural and powder refinement data for  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> structure***Table S2a. Powder and refinement data for  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> structure.*

| Powder Data (T=293K)                              |                                                           |
|---------------------------------------------------|-----------------------------------------------------------|
| Formula                                           | $\alpha$ -BaMn <sub>2</sub> P <sub>2</sub> O <sub>8</sub> |
| Molar weight (g/mol)                              | 437,15                                                    |
| Symmetry                                          | Monoclinic                                                |
| Space group                                       | C 1 2 1 (5)                                               |
| Unit cell (Å) and angle (°)                       | a = 9.09710(4)<br>b=5.18068(2)<br>c = 24.98384(12)        |
| $\beta$ (°)                                       | 90.4107(2)                                                |
| Volume (Å <sup>3</sup> )                          | 1177.437(9)                                               |
| Z                                                 | 6                                                         |
| Data collection                                   |                                                           |
| Equipment                                         | Synchrotron (I11-DIAMOND)                                 |
| $\lambda$ (K $\alpha$ ; Å)                        | 0,824899                                                  |
| Sample Holder                                     | 0,5mm Glass Capillary                                     |
| density calc. (g/cm <sup>3</sup> )                | 3,6991                                                    |
| Sample                                            | Powder                                                    |
| Color                                             | Pale Pink                                                 |
| $\theta$ (min-max) (°)                            | 2,10800 - 92,11200                                        |
| $\mu$ (mm-1 for $\lambda$ (K $\alpha$ =0,824899Å) | 12,695                                                    |
| R <sub>Bragg</sub> (%)                            | 10,9                                                      |

*Table S2b. Atomic Positions & equivalent anisotropic thermal displacement for  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> structure.*

| Atom | Wick. | x           | y           | z           | Ueq (Å <sup>2</sup> ) |
|------|-------|-------------|-------------|-------------|-----------------------|
| Ba1  | 4c    | 0.02273(18) | 0.0502(8)   | 0.33372(9)  | 0.0218(5)             |
| Ba2  | 2a    | 0.00000     | 0.0520(10)  | 0.00000     | 0.0407(10)            |
| Mn1  | 4c    | -0.2804(4)  | 0.0571(11)  | 0.21869(14) | 0.0063(4)             |
| Mn2  | 4c    | -0.1187(4)  | -0.4549(14) | 0.11200(15) | 0.0063(4)             |
| Mn3  | 4c    | 0.1616(5)   | -0.3240(9)  | 0.5545(2)   | 0.0063(4)             |
| P1   | 4c    | 0.1586(4)   | 0.5793(8)   | 0.08829(15) | 0.041(3)              |
| O1_1 | 4c    | 0.1079(7)   | 0.5545(13)  | 0.14692(13) | 0.054(3)              |
| O2_1 | 4c    | 0.1843(7)   | 0.8602(6)   | 0.0748(3)   | 0.054(3)              |
| O3_1 | 4c    | 0.3013(5)   | 0.4229(11)  | 0.0820(3)   | 0.054(3)              |
| O4_1 | 4c    | 0.0399(5)   | 0.4629(12)  | 0.0519(2)   | 0.054(3)              |
| P2   | 4c    | -0.1444(4)  | -0.4690(8)  | 0.24836(15) | 0.015(2)              |
| O1_2 | 4c    | -0.2070(6)  | -0.5375(12) | 0.19245(15) | 0.004(2)              |
| O2_2 | 4c    | -0.2251(6)  | -0.6320(11) | 0.2898(2)   | 0.004(2)              |
| O3_2 | 4c    | 0.0210(3)   | -0.5347(12) | 0.2502(2)   | 0.004(2)              |
| O4_2 | 4c    | -0.1619(6)  | -0.1895(6)  | 0.2598(2)   | 0.004(2)              |
| P3   | 4c    | 0.3348(4)   | 0.0933(7)   | 0.58069(14) | 0.003(2)              |
| O1_3 | 4c    | 0.3464(7)   | -0.0107(12) | 0.52385(14) | 0.046(3)              |
| O2_3 | 4c    | 0.4707(5)   | 0.0186(13)  | 0.6132(2)   | 0.046(3)              |
| O3_3 | 4c    | 0.3144(7)   | 0.3860(6)   | 0.5805(3)   | 0.046(3)              |
| O4_3 | 4c    | 0.1976(5)   | -0.0266(12) | 0.6071(2)   | 0.046(3)              |

### (S3) SEM EDS analysis

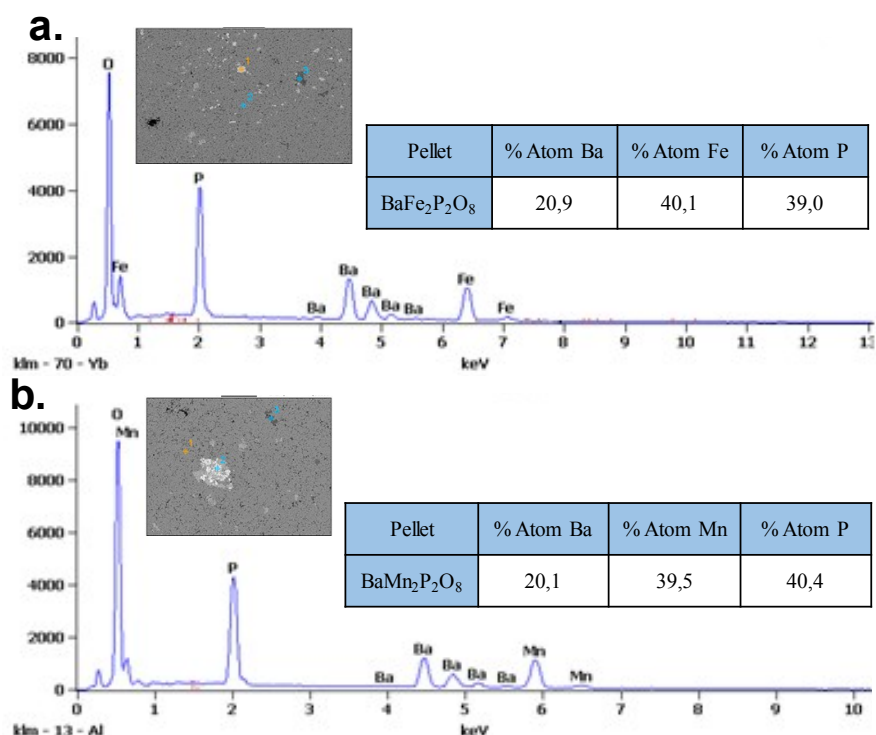


Figure S3. SEM EDS analysis and resulting averaged atomic proportions (%) performed on (a)  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> pellet and (b)  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> pellet.

### (S4) UV-Visible and IR spectroscopies

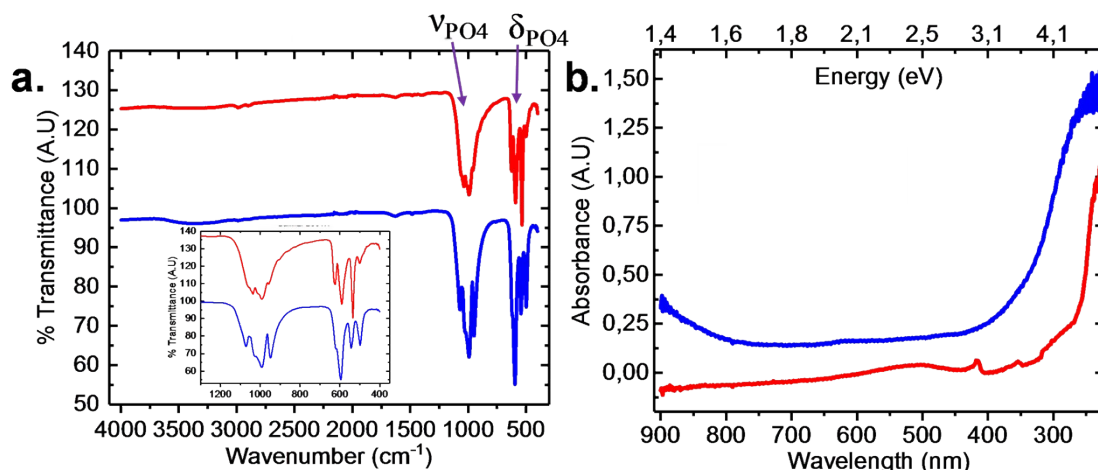
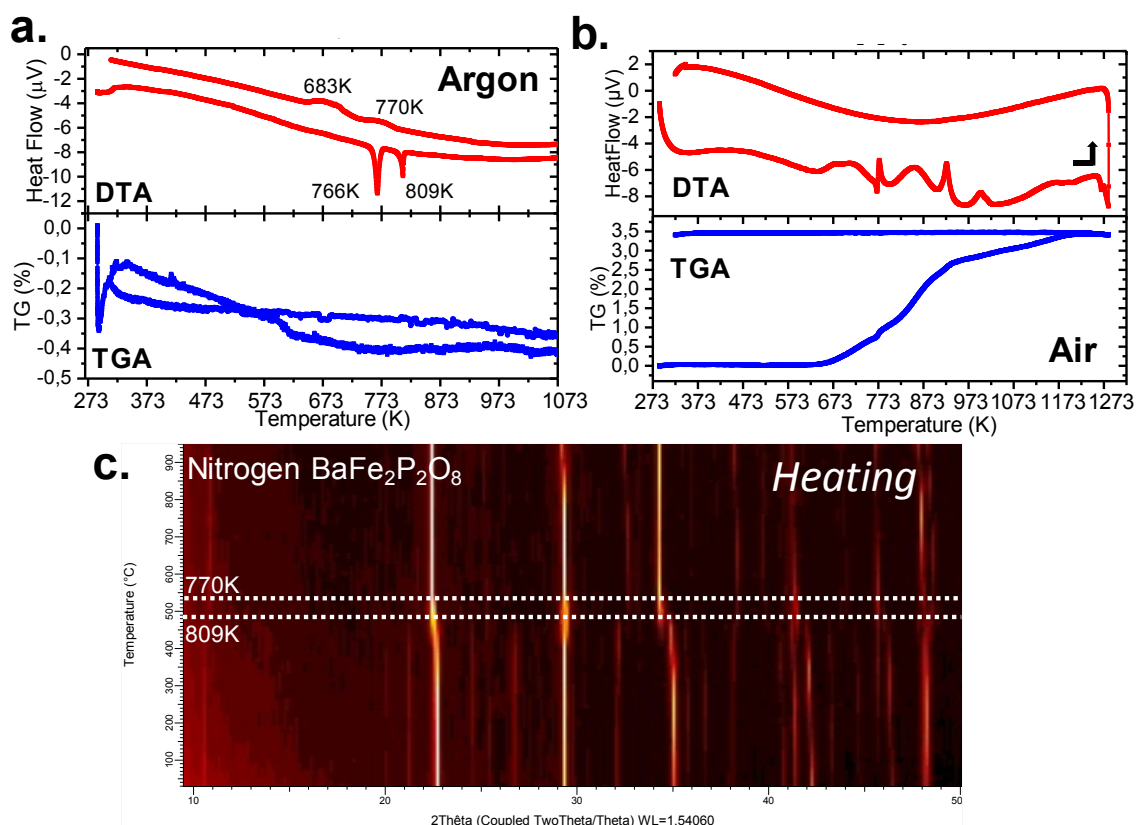
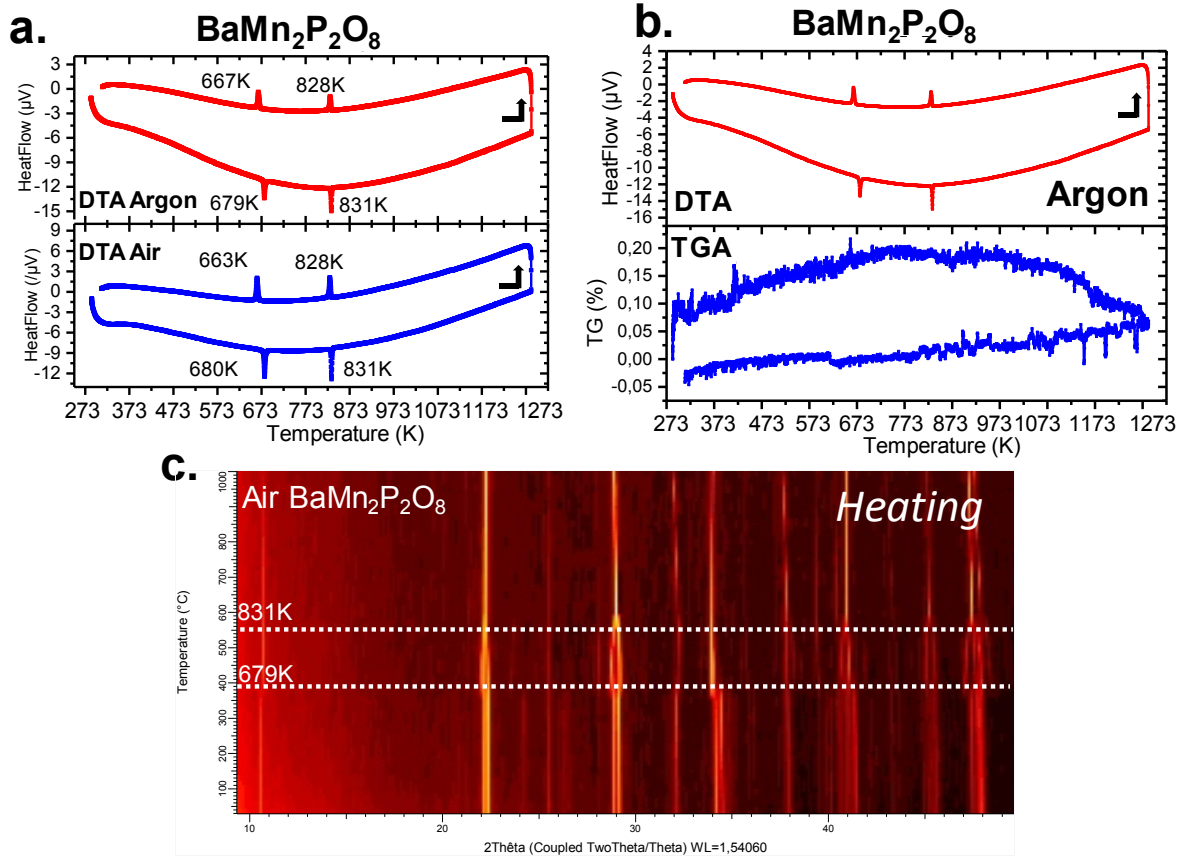


Figure S4. (a) Transmittance Infrared Spectra of  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> (in blue) and  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> (in red). The IR spectra show only evidence of stretching and bending PO<sub>4</sub> vibrations bands. Respectively (1062 cm<sup>-1</sup>, 1039 cm<sup>-1</sup>, 996 cm<sup>-1</sup>, 955 cm<sup>-1</sup> // 627 cm<sup>-1</sup>, 593 cm<sup>-1</sup>, 534 cm<sup>-1</sup>, 499 cm<sup>-1</sup>) for  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> and (1074 cm<sup>-1</sup>, 1029 cm<sup>-1</sup>, 996 cm<sup>-1</sup>, 950 cm<sup>-1</sup> // 622 cm<sup>-1</sup>, 593 cm<sup>-1</sup>, 540 cm<sup>-1</sup>, 499 cm<sup>-1</sup>) for  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub>. (b) Absorbance UV Visible spectroscopies for  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> (in blue) and  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> (in red). Broad transition around 550 nm responsible for the pink shade of the  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> compound.

### (S5) Thermal analysis for $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> and $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub>

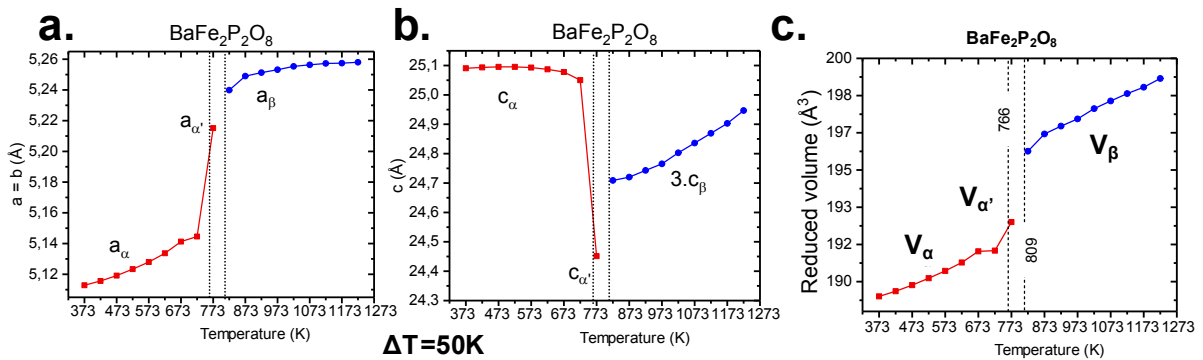


**Figure S5a.** Thermal stability for  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> with (a) DTA and corresponding TGA measurement under flowing Argon atmosphere (red and blue respectively), with highlighting of the two transformation  $\alpha \rightarrow \alpha'$  (766 K),  $\alpha' \rightarrow \beta$  (809 K) and reversibility. No weigh loss along the measurement. (b) DTA and TGA measurement under flowing Air atmosphere (red and blue respectively). The structure decomposes. We notice a weight gain corresponding to the decomposition of the structure, result of iron oxidation. (c) HTXRD evolution ( $\Delta T=50$  K) upon heating under flowing Nitrogen atmosphere with evidence of the two transformation. Reversibility of transformations were also checked upon cooling.

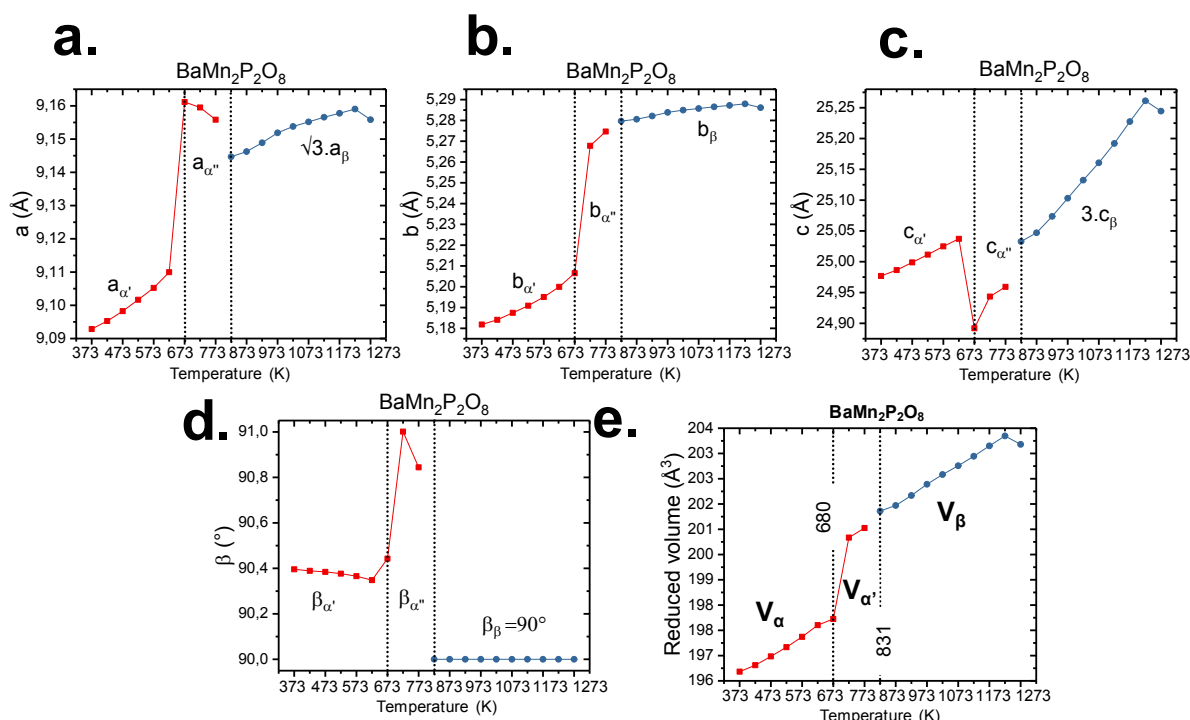


**Figure S5b.** Thermal stability for  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> with (a) DTA under flowing Argon atmosphere (red) and DTA under flowing Air atmosphere (blue), with highlighting of the two transformation  $\alpha \rightarrow \alpha'$  (679 K) and  $\alpha' \rightarrow \beta$  (831 K) and reversibility upon cooling. (b) DTA and TGA measurement under flowing Argon atmosphere (red and blue respectively). No weight loss upon the measurement. (c) HTXRD evolution ( $\Delta T=50$  K) upon heating under flowing Air atmosphere with evidence of the two transformation. Reversibility of transformations were also checked upon cooling.

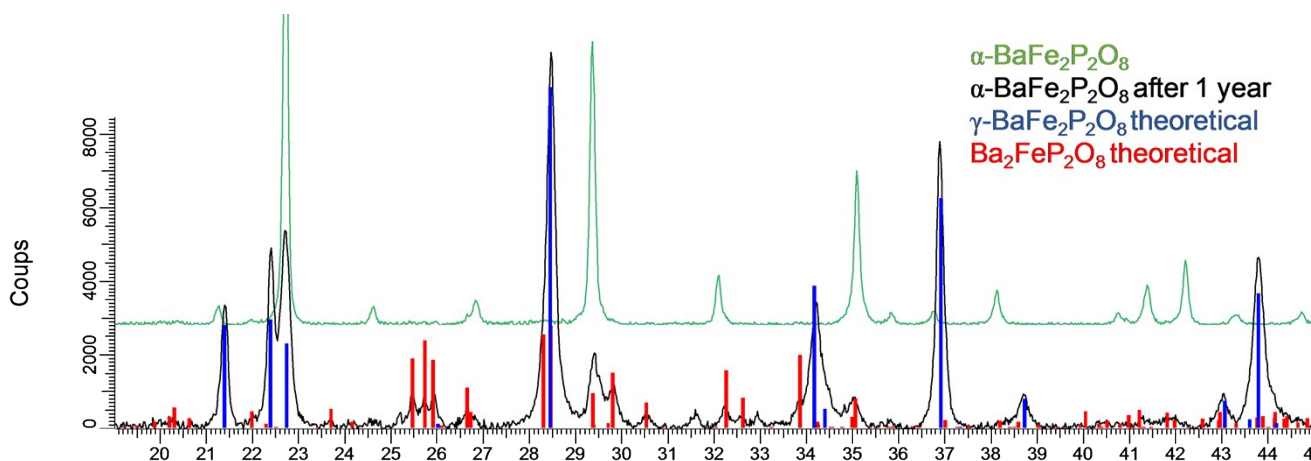
**(S6) Cell parameters evolution and phase transformation upon heating for  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> and  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub>.**



**Figure S6a.** Cell parameters evolution upon heating under nitrogen atmosphere for  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> with (a)  $a$  parameter evolution (Å), (b)  $c$  parameter evolution (Å) and (c) reduced volume evolution (Å<sup>3</sup>). Values obtained from “le Bail” refinement of previous HTXRD datas ( $\Delta T=50$  K).



**Figure S6b.** Cell parameters evolution from monoclinic (in red) to trigonal structure (in blue) upon heating under nitrogen atmosphere for  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> with (a) *a* parameter evolution (Å), (b) *b* parameter evolution (Å), (c) *c* parameter evolution (Å), (d)  $\beta$  parameter evolution (°) and (e) reduced volume evolution (Å<sup>3</sup>). Values obtained from “le Bail” refinement of HTXRD datas ( $\Delta T=50$  K).



#### (S7) Metastability in $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub>

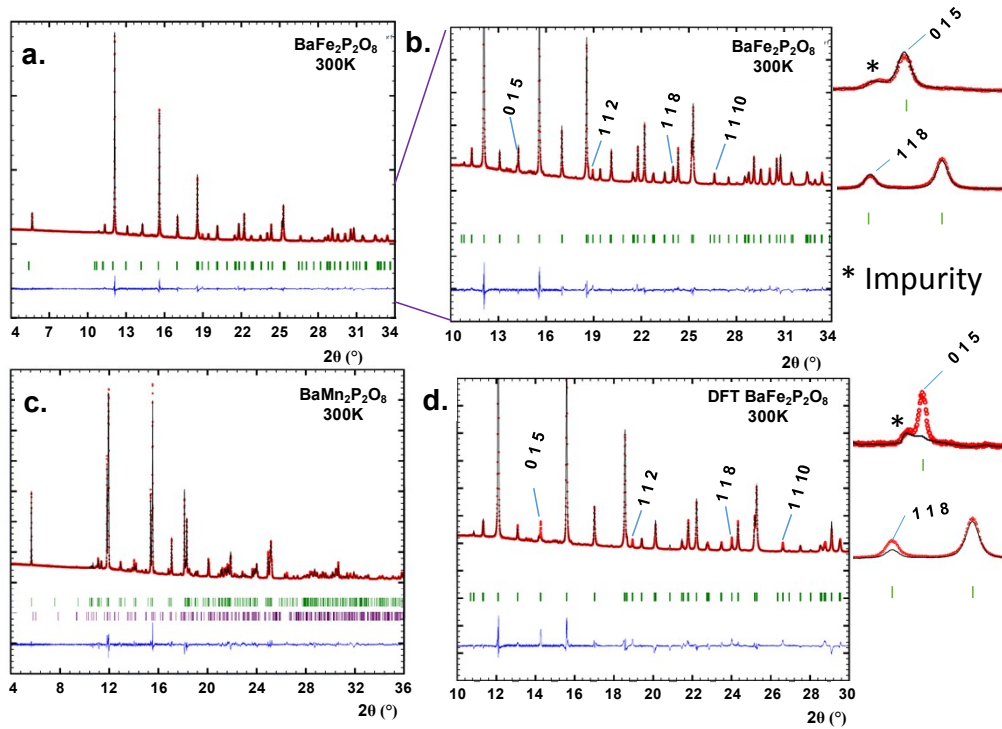
**Figure S7.**  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> to  $\gamma$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> in one year at room temperature and pressure. “Fresh”  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> experimental diagram show in green, “1-year-old”  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> experimental diagram in black, theoretical  $\gamma$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> in blue, and theoretical Ba<sub>2</sub>FeP<sub>2</sub>O<sub>8</sub> in red.

#### (S8) Phase transition in BaM<sub>2</sub>P<sub>2</sub>O<sub>8</sub> systems (M= Co, Fe, Mn)

**Table S8a.** Sum up table for phase transition in BaM<sub>2</sub>P<sub>2</sub>O<sub>8</sub> systems (M= Co, Fe, Mn) with corresponding details about crystallographic structure data.

|                                                   |            | T °K | S.G.               | Z | a (Å)                                         | b (Å)      | c (Å)       | $\beta$ (°)                           | Volume (Å <sup>3</sup> ) | $\rho$ (g/cm <sup>3</sup> ) |
|---------------------------------------------------|------------|------|--------------------|---|-----------------------------------------------|------------|-------------|---------------------------------------|--------------------------|-----------------------------|
| <b>BaCo<sub>2</sub>P<sub>2</sub>O<sub>8</sub></b> | $\alpha$   | 293  | P21/a              | 2 | 9,2110(3)                                     | 5,0040(2)  | 8,0851(3)   | 92,7370(10)                           | 372,23                   | 3,97                        |
|                                                   | $\alpha'$  | -    | -                  | - | -                                             | -          | -           | -                                     | -                        | -                           |
|                                                   | $\alpha''$ | 873  | P21/a              | 2 | 8,2395(6)                                     | 5,1739(4)  | 9,0055(5)   | 91,155(3)                             | 383,83                   | 3,85                        |
|                                                   | $\beta$    | 1173 | P-3                | 1 | 5,22264(4)                                    | 5,22264(4) | 8,26062(10) | 90                                    | 195,13                   | 3,79                        |
|                                                   | $\gamma$   | 298  | R-3                | 3 | 4,8554(6)                                     | 4,8554(6)  | 23,2156(17) | 90                                    | 473,98                   | 4,68                        |
|                                                   | $\epsilon$ |      | P21/c              |   | Magnetic, Resistivity, dielectric transitions |            |             |                                       |                          |                             |
| <b>BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub></b> | $\alpha$   | 293  | P3 <sub>1</sub> 21 | 3 | 5,1140(1)                                     | 5,1140(1)  | 25,1108(1)  | 90                                    | 568,75                   | 3,84                        |
|                                                   | $\alpha'$  | 773  | P3 <sub>1</sub> 21 | 3 | 5,2151(3)                                     | 5,2151(3)  | 24,4512(4)  | 90                                    | 578,01                   | 3,78                        |
|                                                   | $\beta$    | 1173 | P-3                | 1 | 5,2580(2)                                     | 5,2580(2)  | 8,3156(5)   | 90                                    | 199,10                   | 3,66                        |
|                                                   | $\gamma$   | 293  | R-3                | 3 | 4,8730(2)                                     | 4,8730(2)  | 23,368(2)   | 90                                    | 480,56                   | 4,55                        |
|                                                   | $\gamma'$  | 100  | P-1                | 1 | 4,8656(8)                                     | 4,8584(8)  | 8,2481(11)  | 106,850(7)<br>107,012(7)<br>60,333(7) | 159,52                   | 4,57                        |
| <b>BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub></b> | HP         | 293  | P21/a              | 2 | 9,2830(12)                                    | 4,9783(6)  | 8,1326(10)  | 94,106(7)                             | 374,87                   | 3,87                        |
|                                                   | $\alpha$   | 293  | C2                 | 6 | 9,09740(1)                                    | 5,1808(1)  | 24,9849(1)  | 90,4112(2)                            | 1177,55                  | 3,70                        |
|                                                   | $\alpha'$  | 773  | C2                 | 6 | 9,1558(3)                                     | 5,2747(2)  | 24,9592(3)  | 90,8443(2)                            | 1205,25                  | 3,61                        |
|                                                   | $\beta$    | 1273 | P-3                | 1 | 5,2861(3)                                     | 5,2861(3)  | 8,4148(5)   | 90                                    | 203,63(2)                | 3,56                        |

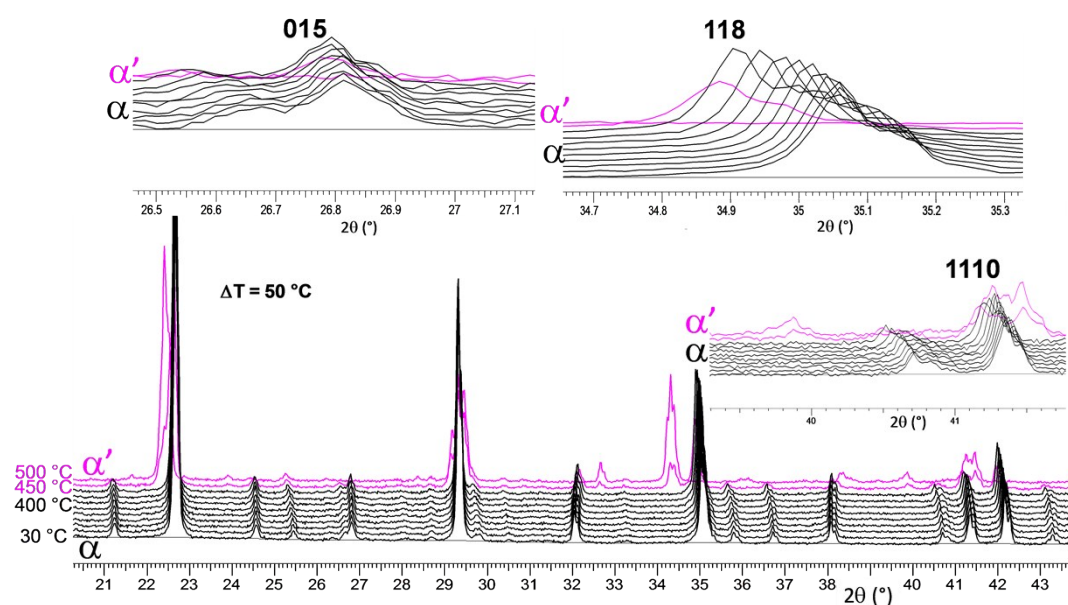
(S9)



Synchrotron Diffraction data Refinement

*Figure S9. Synchrotron data refinement with (a)  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> model refined (b) enlargement for  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> (c)  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> model refined and (d) relaxed DFT calculations model for  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> on experimental synchrotron data. In the latter, the missing intensities (in particular 015 and 118) are highlighted on the right. The green mark corresponds to the alpha phase, the purple to the Ba<sub>2</sub>MnP<sub>2</sub>O<sub>8</sub> impurities refined in the case of  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> but excluded in the case of  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> (we were not able to refine it properly).*

#### (S10) HTXRD vs relaxed model



*Figure S10.  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> HTXRD between 30 °C and 501 °C. From 30 to 400 °C we're in the alpha form (black lines), from 400 °C to 501 °C (magenta lines) we're in the alpha' form. In the latter, we see loss in intensity on characteristic peaks in agreement with the relaxed structure model from DFT.*

#### (S11) Details about DFT calculations

*Table S11a. Comparison of system total Energy (in eV/FU) between  $\alpha$ -BaM<sub>2</sub>P<sub>2</sub>O<sub>8</sub> and  $\gamma$ -BaM<sub>2</sub>P<sub>2</sub>O<sub>8</sub> (M = Fe, Co, Mn) structure. We used our refined model from synchrotron data for  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> and  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub>, and ICSD structure for the others. On the upper part of the tables, only the non-coherent  $\gamma$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> structure was fully relaxed, starting from the closest  $\gamma$ -BaCo<sub>2</sub>P<sub>2</sub>O<sub>8</sub> structure. On the bottom part, values for the relaxed  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> and  $\gamma$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub>, cell parameters and volume constant.*

| System                                                  | Structure                     | U and<br>k points mesh                                    | Total Energy<br>(eV/FU) | Difference<br>(eV/FU) |
|---------------------------------------------------------|-------------------------------|-----------------------------------------------------------|-------------------------|-----------------------|
| BaFe <sub>2</sub> P <sub>2</sub> O <sub>8</sub>         | $\alpha$ , P3 <sub>1</sub> 21 | U= 6 eV<br>10x10x2 <i>k</i> mesh<br>(104 <i>k</i> points) | -90,118                 | 0,850                 |
|                                                         | $\gamma$ , R-3                | U= 6 eV<br>12x12x2 <i>k</i> mesh<br>(52 <i>k</i> points)  | -90,968                 |                       |
| BaCo <sub>2</sub> P <sub>2</sub> O <sub>8</sub>         | $\alpha$ , P21/a              | U = 4 eV<br>6x10x8 <i>k</i> mesh<br>(244 <i>k</i> points) | -90,885                 | -1,070                |
|                                                         | $\gamma$ , R-3                | U = 4 eV<br>12x12x2 <i>k</i> mesh<br>(52 <i>k</i> points) | -89,814                 |                       |
| BaMn <sub>2</sub> P <sub>2</sub> O <sub>8</sub>         | $\alpha$ , C2                 | U = 4 eV<br>2x5x1 <i>k</i> mesh<br>(44 <i>k</i> points)   | -97,002                 | -1,012                |
|                                                         | $\gamma$ , R-3                | U = 4 eV<br>6x6x1 <i>k</i> mesh<br>after full relaxation  | -95,990                 |                       |
| After relaxations with unit cell parameters constrained |                               |                                                           |                         |                       |
| BaFe <sub>2</sub> P <sub>2</sub> O <sub>8</sub>         | $\alpha$ , P3 <sub>1</sub> 21 | U= 6 eV<br>10x10x2 <i>k</i> mesh<br>(104 <i>k</i> points) | -92,610                 | -1,623                |
|                                                         | $\gamma$ , R-3                | U= 6 eV<br>6x6x1 <i>k</i> mesh<br>(8 <i>k</i> points)     | -90,986                 |                       |

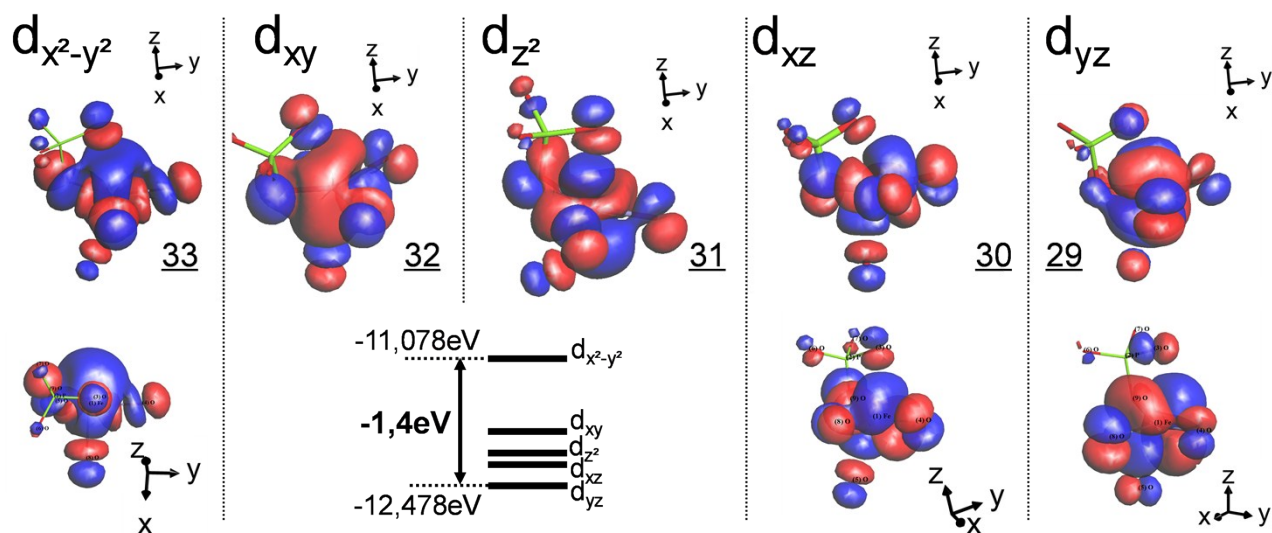
*Table S11b. To the left, comparison of Fe-O and P-O distances between refined  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> model from the synchrotron data, and relaxed  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> model from DFT calculations. To the right, comparison of Fe-O and P-O distances between refined  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> model from the synchrotron data, and relaxed  $\alpha$ -BaMn<sub>2</sub>P<sub>2</sub>O<sub>8</sub> model from DFT calculations.*

| $\alpha$ -<br>BaFe <sub>2</sub> P <sub>2</sub> O <sub>8</sub> | Refined        | DFT         | $\alpha$ -<br>BaMn <sub>2</sub> P <sub>2</sub> O <sub>8</sub> | Refined<br>Mn  | DFT         | $\alpha$ -<br>BaMn <sub>2</sub> P <sub>2</sub> O <sub>8</sub> | Refined<br>P   | DFT<br>P    |
|---------------------------------------------------------------|----------------|-------------|---------------------------------------------------------------|----------------|-------------|---------------------------------------------------------------|----------------|-------------|
| Fe-O1 (Å)                                                     | 2,057(4)       | 1,947       | Mn1—O1_1 (Å)                                                  | 2.055(5)       | 1,943       | P1—O1_1 (Å)                                                   | 1.544(5)       | 1,610       |
| Fe-O1 (Å)                                                     | 2,524(6)       | 1,984       | Mn1—O1_2 (Å)                                                  | 2.301(8)       | 1,976       | P1—O2_1 (Å)                                                   | 1.512(5)       | 1,553(3)    |
| Fe-O3 (Å)                                                     | 2,072(4)       | 2,022       | Mn1—O2_2 (Å)                                                  | 2.448(7)       | 2,125       | P1—O3_1 (Å)                                                   | 1.539(6)       | 1,540       |
| Fe-O2 (Å)                                                     | 2,589(6)       | 2,028       | Mn1—O3_2 (Å)                                                  | 2.032(5)       | 2,053       | P1—O4_1 (Å)                                                   | 1.530(6)       | 1,565       |
| Fe-O4 (Å)                                                     | 1,767(4)       | 2,032       | Mn1—O4_2 (Å)                                                  | 1.958(6)       | 2,054       |                                                               | <b>5,04(4)</b> | <b>4,43</b> |
| Fe-P (Å)                                                      | 2,641(5)       | 2,601       |                                                               | <b>2,06(2)</b> | <b>2,66</b> | P2—O1_2 (Å)                                                   | 1.546(6)       | 1,612       |
| Fe-P (Å)                                                      | 3,041(4)       | 3,171       | Mn2—O1_1 (Å)                                                  | 2.233(7)       | 1,997       | P2—O2_2 (Å)                                                   | 1.528(7)       | 1,567       |
| Fe-P (Å)                                                      | 3,298(4)       | 3,185       | Mn2—O2_1 (Å)                                                  | 2.229(8)       | 2,067       | P2—O3_2 (Å)                                                   | 1.543(5)       | 1,554       |
|                                                               | <b>1,99(2)</b> | <b>2,43</b> | Mn2—O3_1 (Å)                                                  | 2.217(9)       | 2,072       | P2—O4_2 (Å)                                                   | 1.485(5)       | 1,563       |
| P1-O3 (Å)                                                     | 1,559(5)       | 1,539       | Mn2—O4_1 (Å)                                                  | 2.133(6)       | 2,098       |                                                               | <b>5,13(4)</b> | <b>4,43</b> |
| P1-O2 (Å)                                                     | 1,476(6)       | 1,553       | Mn2—O1_2 (Å)                                                  | 2.212(6)       | 1,937       | P3—O1_3 (Å)                                                   | 1.523(5)       | 1,613       |
| P1-O4 (Å)                                                     | 1,578(7)       | 1,568       |                                                               | <b>1,64(2)</b> | <b>2,62</b> | P3—O2_3 (Å)                                                   | 1.524(6)       | 1,551       |
| P1-O1 (Å)                                                     | 1,530(4)       | 1,596       | Mn3—O1_3 (Å)                                                  | 2.463(8)       | 1,968       | P3—O3_3 (Å)                                                   | 1.528(5)       | 1,536       |
|                                                               | <b>4,84(3)</b> | <b>4,46</b> | Mn3—O1_3 (Å)                                                  | 2.184(6)       | 1,943       | P3—O4_3 (Å)                                                   | 1.546(6)       | 1,572       |
|                                                               |                |             | Mn3—O2_3 (Å)                                                  | 2.422(7)       | 2,087       |                                                               | <b>5,06(4)</b> | <b>4,42</b> |
|                                                               |                |             | Mn3—O3_3 (Å)                                                  | 2.144(7)       | 2,060       |                                                               |                |             |
|                                                               |                |             | Mn3—O4_3 (Å)                                                  | 2.050(7)       | 2,124       |                                                               |                |             |
|                                                               |                |             |                                                               | <b>1,60(2)</b> | <b>2,62</b> |                                                               |                |             |

*Table S11c. Fe-O bond distances and associated Integral COHP for spins ( $\uparrow$ ) and ( $\downarrow$ ), negative values of ICOHP are indicating net bonding character.*

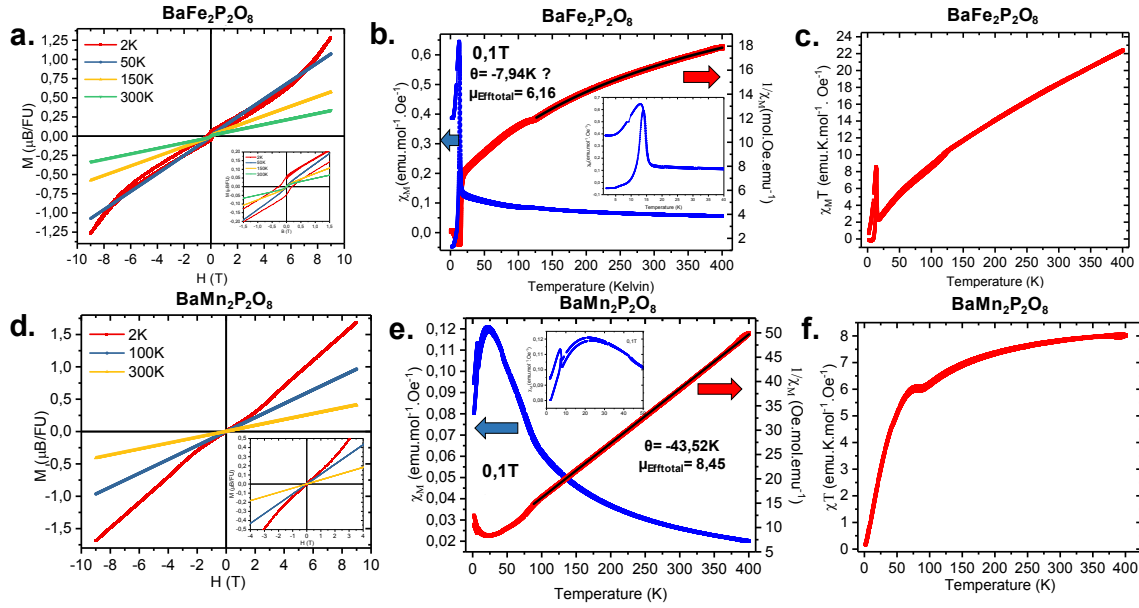
| Bond  | Distance (Å) | ICOHP spin ( $\uparrow$ ) (eV) | ICOHP spin ( $\downarrow$ ) (eV) |
|-------|--------------|--------------------------------|----------------------------------|
| Fe1-O | 1.767        | <b>-1.04414</b>                | <b>-1.62688</b>                  |
| Fe1-O | 2.057        | -1.00795                       | -1.21956                         |
| Fe1-O | 2.072        | -0.89122                       | -1.09690                         |
| Fe1-O | 2.524        | -0.84155                       | -0.93160                         |
| Fe1-O | 2.589        | -0.54278                       | -0.62248                         |

**(S12) Details about Orbitals representation for  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub>**



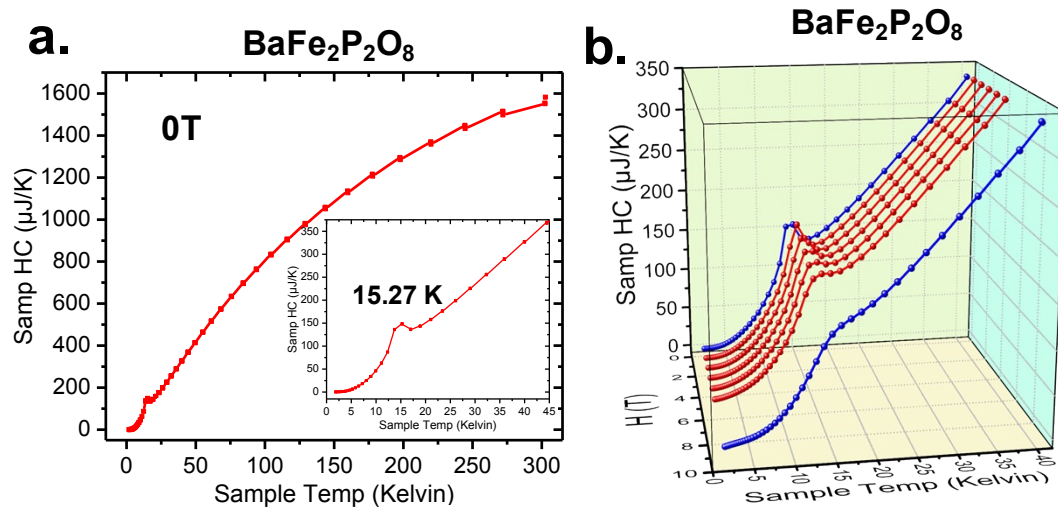
*Figure S12. 3D MO d Fe orbitals simulation with corresponding name and energies for  $\alpha$ -BaFe<sub>2</sub>P<sub>2</sub>O<sub>8</sub> structure.*

**(S13) Additional Magnetic Measurements**



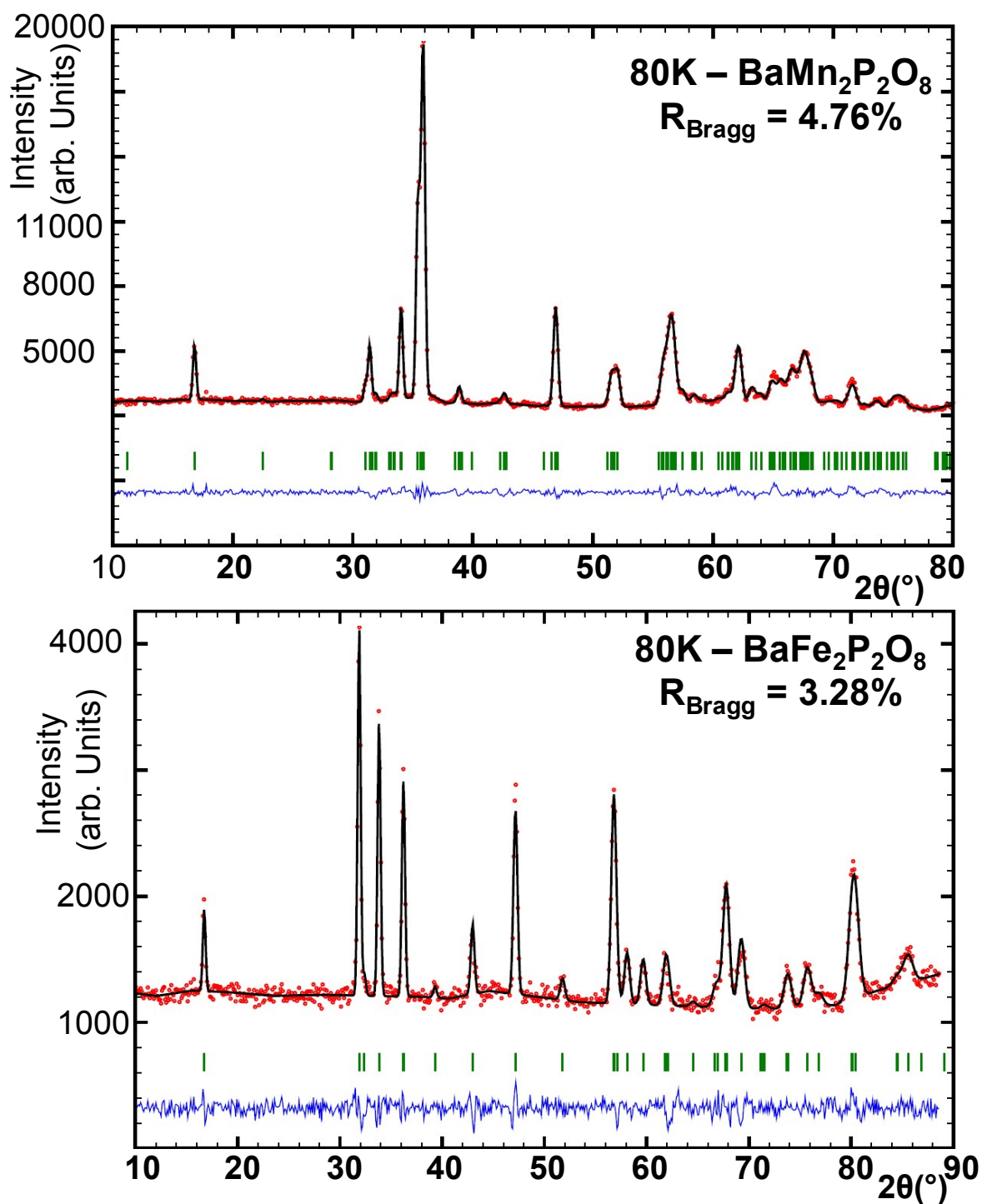
**Figure S13.** Magnetic measurements data for  $\alpha$ - $\text{BaFe}_2\text{P}_2\text{O}_8$  with (a)  $M$  vs  $H$  at 2 K, 50 K, 150 K, 300 K, between -9 T and 9 T (b) ZFC/FC  $\chi_M$  and  $1/\chi_M$  (blue and red respectively) from 400 K to 2 K, and (c) corresponding  $\chi_M T$ . We recall the presence of  $\text{Fe}_3\text{O}_4$  impurities in the sample, proved by the Verwey phase transition at 125 K. Magnetic measurements data for  $\alpha$ - $\text{BaMn}_2\text{P}_2\text{O}_8$  with (d)  $M$  vs  $H$  at 2 K, 100 K, 300 K, between -9 T and 9 T (b) ZFC/FC  $\chi_M$  and  $1/\chi_M$  (blue and red respectively) from 400 K to 2 K, and (c) corresponding  $\chi_M T$ .

#### (S14) Specific Heat measurement



**Figure S14.** (a)  $\alpha$ - $\text{BaFe}_2\text{P}_2\text{O}_8$  specific heat measurement between 300 K and 2 K at 0 T, (b)  $\alpha$ - $\text{BaFe}_2\text{P}_2\text{O}_8$  specific heat measurement between 40 K and 2 K under different field from 0 to 9 T.

#### (S15) Powder Neutron Diffraction refinement



*Figure S15.  $\alpha\text{-BaMn}_2\text{P}_2\text{O}_8$  and  $\alpha\text{-BaFe}_2\text{P}_2\text{O}_8$  powder neutron diffraction Rietveld refinement (a and b respectively) at 80K with our synchrotron refined model. The green mark corresponds to Bragg peaks, the red curves to the experimental measured points, the black curves to the intensity following our model, and the blue curves to the difference between them. At 80 K we are above the  $T_N$  of both compounds (so there is only structural contribution to the intensities measured).*