

Supplementary information

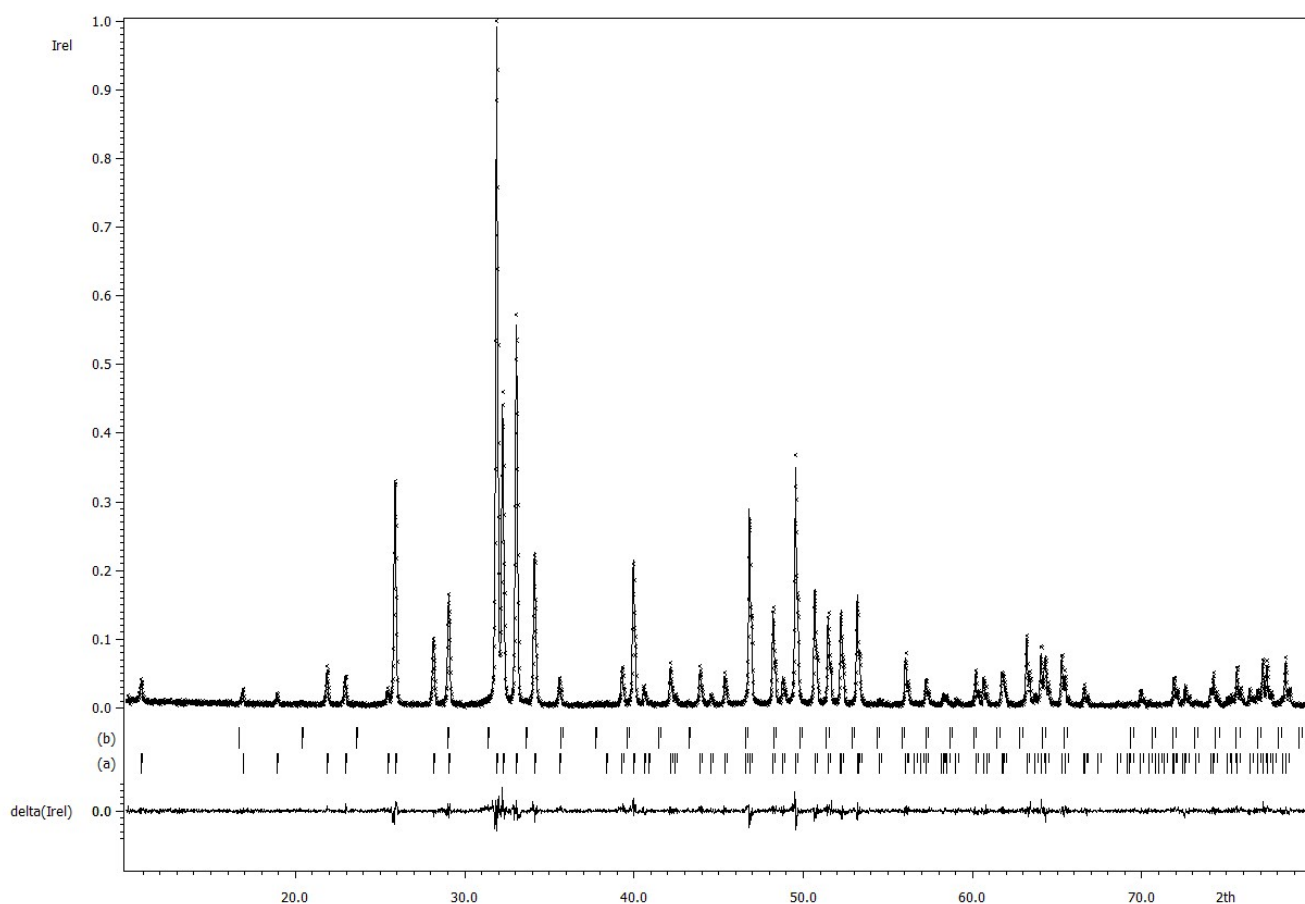


Figure S1. Powder X-ray diffraction pattern of **1**. Observed (crosses), calculated (solid line) and difference (solid line below) plots. Positions of Bragg reflections are shown as strokes underneath: (a) the main apatite-type phase and (b) Dy₂O₃ (0.18 wt. %). Apatite-type phase lattice: space group P6₃/m, $a = 9.3878(2)$ Å, $c = 6.8842(1)$ Å.

Table S1. Atomic parameters and thermal displacement parameters of **1**. $R_{wp} = 0.139$, $R_{all} = 0.024$.

Atom	Ca(1)	Ca(2)	P	O(1) ^{a)}	O(2)	O(3)	[O,F](4)	Dy ^{b)}
Site	4f	6h	6h	6h	6h	12i	4e	6h
SOF	1	0.9833	1	1	1	1	0.25, 0.25	0.0167
x	1/3	0.0070(4)	0.3987(4)	0.3283(8)	0.5875(9)	0.3426(7)	0	0.0070(4)
y	2/3	0.2500(3)	0.3680(5)	0.4849(8)	0.4665(9)	0.2580(6)	0	0.2500(3)
z	0.0027(5)	1/4	1/4	1/4	1/4	0.0696(7)	0.209(2)	1/4
U_{eq} , U_{iso}	0.018(2)	0.017(2)	0.015(2)	0.014(3)	0.014(3)	0.014(3)	0.014(3)	0.017(2)

^{a)} U_{iso} for O(1), O(2), O(3), and [O,F](4) were constrained to equal values.

^{b)} Dy is located at the Ca(2) site.

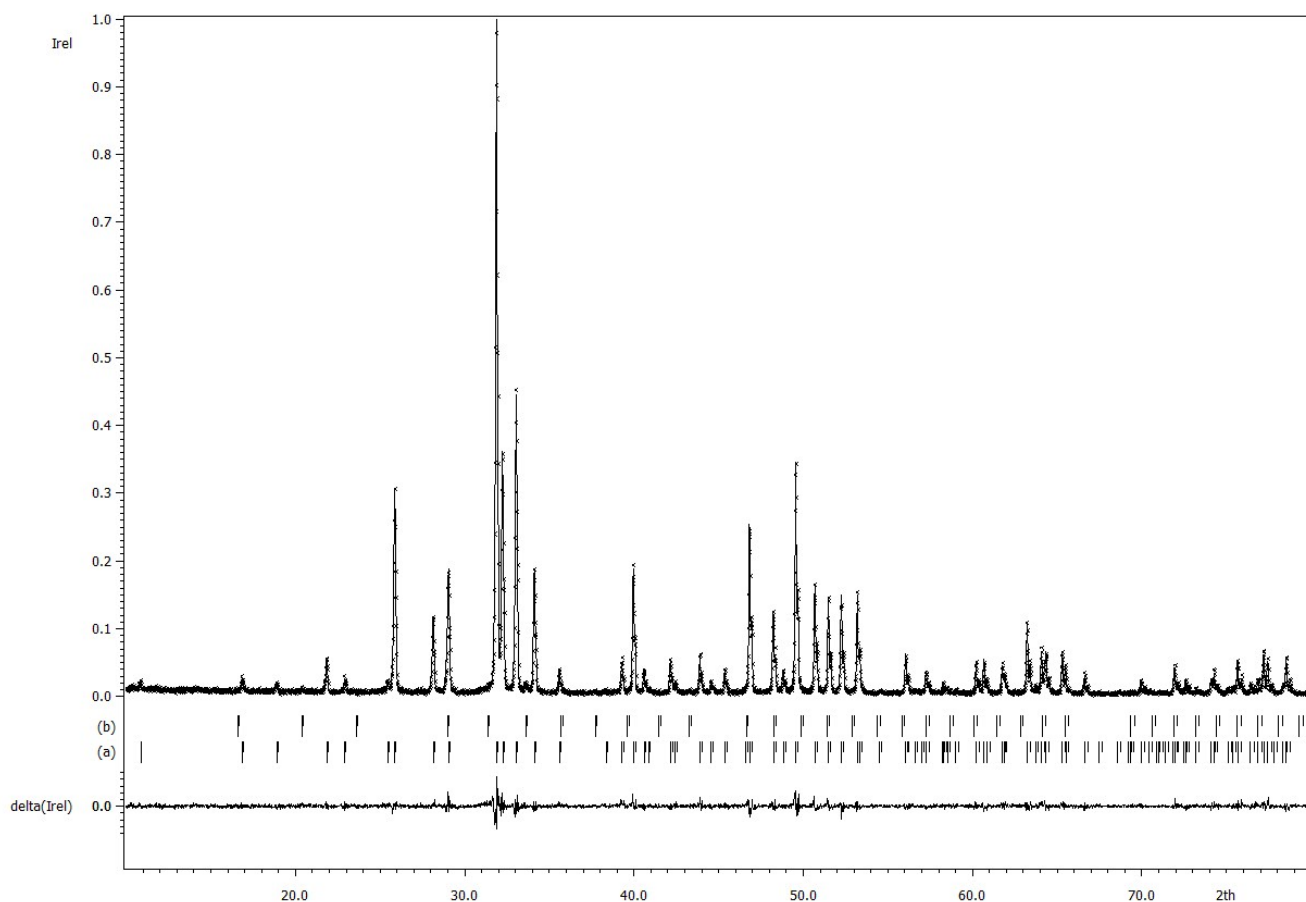


Figure S2. Powder X-ray diffraction pattern of **2**. Observed (crosses), calculated (solid line) and difference (solid line below) plots. Positions of Bragg reflections are shown as strokes underneath: (a) the main apatite-type phase and (b) Dy_2O_3 (0.74 wt. %). Apatite-type phase lattice: space group $P6_3/m$, $a = 9.3792(2)$ Å, $c = 6.8781(2)$ Å.

Table S2. Atomic parameters and thermal displacement parameters of **2**. $R_{\text{wp}} = 0.137$, $R_{\text{all}} = 0.023$.

Atom	Ca(1) ^{a)}	Ca(2)	P	O(1) ^{b)}	O(2)	O(3)	[O,F](4)	Dy ^{c)}
Site	4f	6h	6h	6h	6h	12i	4e	6h
SOF	1	0.930(3)	1	1	1	1	0.25, 0.25	0.070(3)
<i>x</i>	1/3	0.0061(4)	0.4000(5)	0.3284(10)	0.5883(10)	0.3424(7)	0	0.0061(4)
<i>y</i>	2/3	0.2450(3)	0.3699(5)	0.4855(9)	0.4690(10)	0.2565(7)	0	0.2450(3)
<i>z</i>	0.0012(6)	1/4	1/4	1/4	1/4	0.0686(7)	0.219(3)	1/4
U_{iso}	0.015(2)	0.015(2)	0.013(2)	0.013(2)	0.013(2)	0.013(2)	0.013(2)	0.015(2)

^{a)} U_{iso} for Ca(1), Ca(2), and Dy were constrained to equal values.

^{b)} U_{iso} for O(1), O(2), O(3), and [O,F](4) were constrained to equal values.

^{c)} Dy is located at the Ca(2) site.

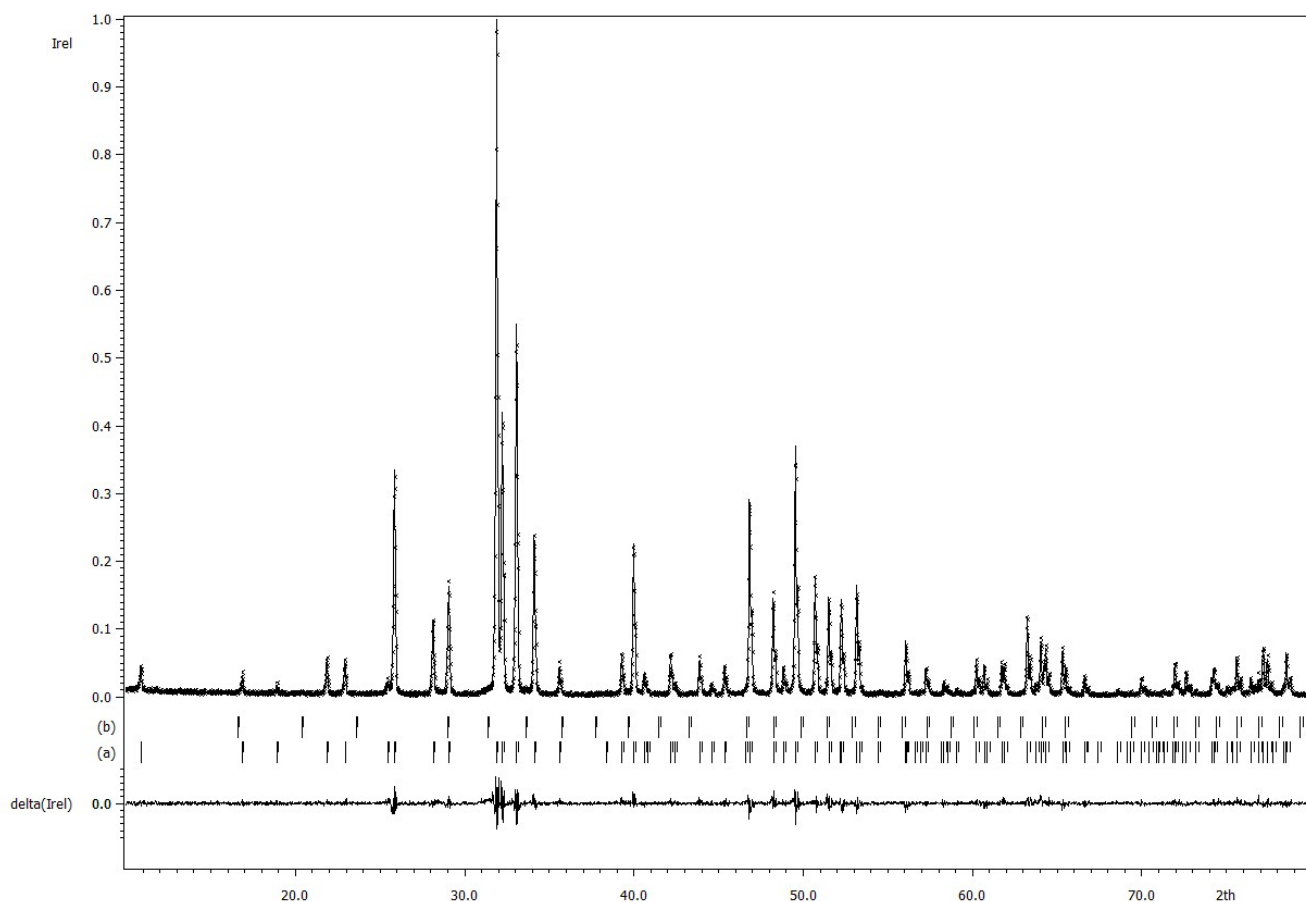


Figure S3. Powder X-ray diffraction pattern of **3**. Observed (crosses), calculated (solid line) and difference (solid line below) plots. Positions of Bragg reflections are shown as strokes underneath: (a) the main apatite-type phase and (b) Dy_2O_3 (0.27 wt. %). Apatite-type phase lattice: space group $P6_3/m$, $a = 9.3775(2)$ Å, $c = 6.8840(2)$ Å.

Table S3. Atomic parameters and thermal displacement parameters of **3**. $R_{\text{wp}} = 0.143$, $R_{\text{all}} = 0.024$.

Atom	Ca(1)	Ca(2)	P	O(1) ^{a)}	O(2)	O(3)	[O,F](4)	Dy ^{b)}
Site	4f	6h	6h	6h	6h	12i	4e	6h
SOF	1	0.9833	1	1	1	1	0.025, 0.475	0.0167
x	1/3	0.0066(4)	0.3984(5)	0.3264(10)	0.5880(10)	0.3403(8)	0	0.0066(4)
y	2/3	0.2483(4)	0.3685(5)	0.4829(9)	0.4655(10)	0.2560(7)	0	0.2483(4)
z	0.0014(6)	1/4	1/4	1/4	1/4	0.0705(8)	0.215(3)	1/4
U_{eq} , U_{iso}	0.015(3)	0.016(3)	0.013(3)	0.010(3)	0.010(3)	0.010(3)	0.010(3)	0.016(3)

^{a)} U_{iso} for O(1), O(2), O(3), and [O,F](4) were constrained to equal values.

^{b)} Dy is located at the Ca(2) site.

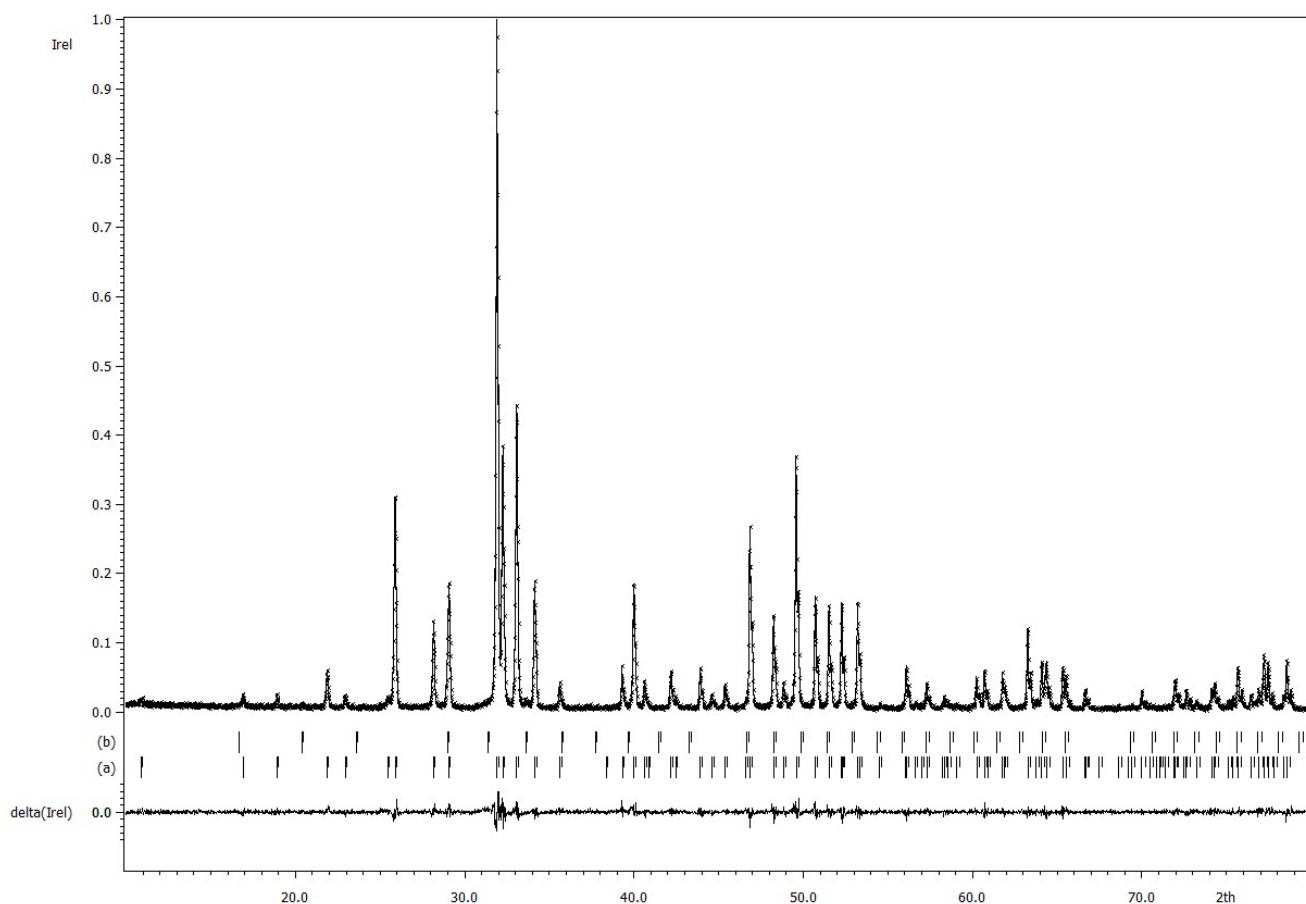


Figure S4. Powder X-ray diffraction pattern of **4**. Observed (crosses), calculated (solid line) and difference (solid line below) plots. Positions of Bragg reflections are shown as strokes underneath: (a) the main apatite-type phase and (b) Dy_2O_3 (0.58 wt. %). Apatite-type phase lattice: space group $P6_3/m$, $a = 9.3778(2)$ Å, $c = 6.8791(2)$ Å.

Table S4. Atomic parameters and thermal displacement parameters of **4**. $R_{\text{wp}} = 0.139$, $R_{\text{all}} = 0.019$.

Atom	Ca(1) ^{a)}	Ca(2)	P	O(1) ^{b)}	O(2)	O(3)	[O,F](4)	Dy ^{c)}
Site	4f	6h	6h	6h	6h	12i	4e	6h
SOF	1	0.928(4)	1	1	1	1	0.125, 0.375	0.072(4)
x	1/3	0.0066(4)	0.3993(6)	0.3267(10)	0.5866(10)	0.3417(8)	0	0.0066(4)
y	2/3	0.2450(3)	0.3699(5)	0.4851(9)	0.4674(10)	0.2561(7)	0	0.2450(3)
z	0.0006(6)	1/4	1/4	1/4	1/4	0.0691(8)	0.217(3)	1/4
U_{eq} , U_{iso}	0.011(3)	0.011(3)	0.011(3)	0.009(3)	0.009(3)	0.009(3)	0.009(3)	0.011(3)

^{a)} U_{iso} for Ca(1), Ca(2), and Dy were constrained to equal values.

^{b)} U_{iso} for O(1), O(2), O(3), and [O,F](4) were constrained to equal values.

^{c)} Dy is located at the Ca(2) site.

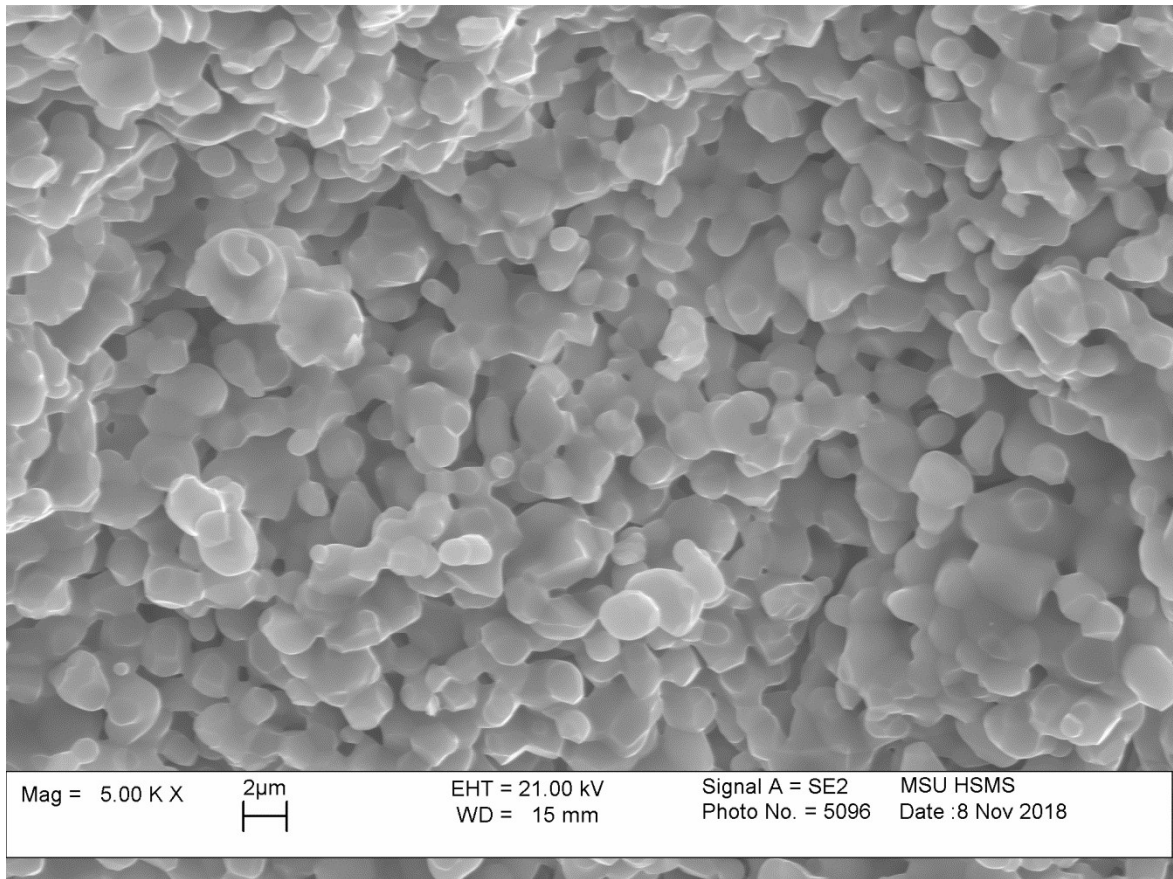
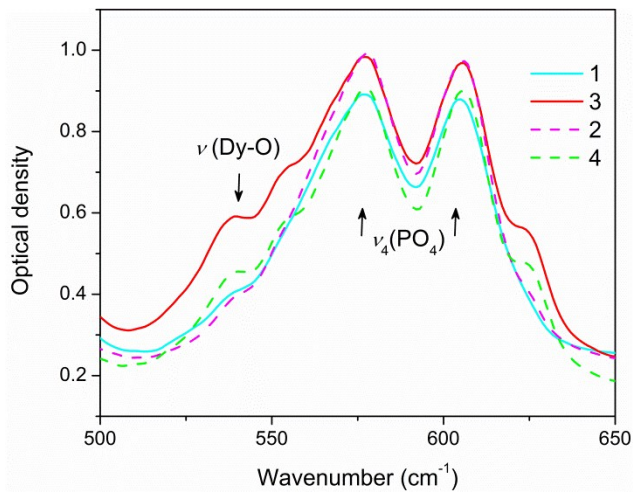
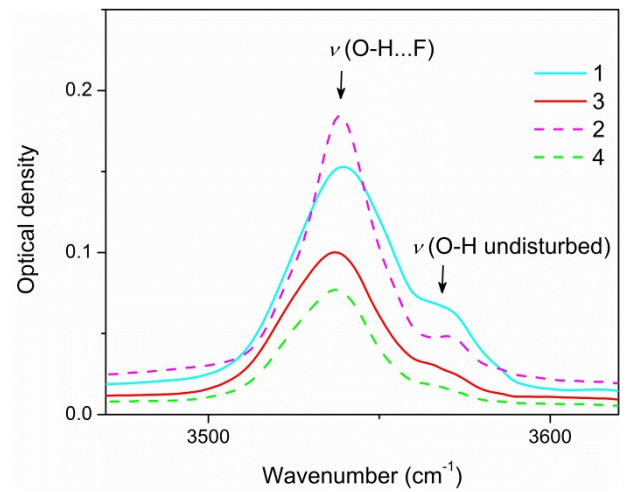


Figure S5. Scanning electron microscopy image of the fractured surface of sample 2.



(a)



(b)

Figure S6. Diffuse reflectance FT-IR spectra (recalculated to optical density) of samples prepared, (a) – the region with Dy-O stretching vibrations, (b) – the region with OH stretching vibrations.

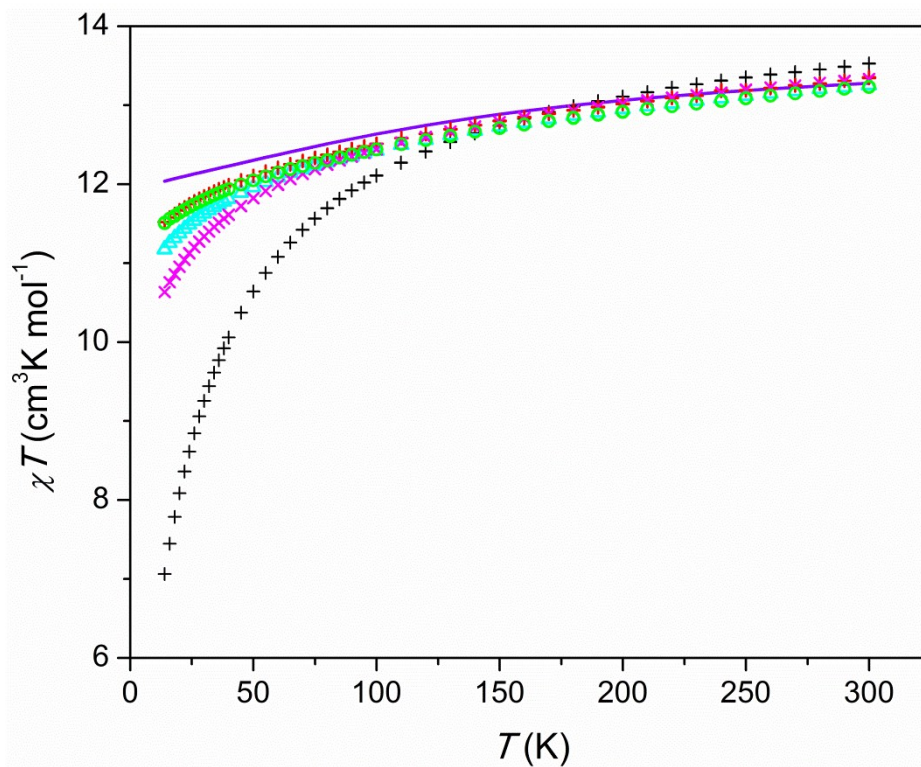


Figure S7. Temperature dependence of χT (per mol of Dy) under a magnetic field of 1 kOe. Symbols, blue triangles – 1, red pluses – 2, magenta crosses – 3, green circles – 4, black crosses – Dy_2O_3 . Violet line – an expected $\chi T(T)$ for DyO^+ calculated for $\text{Ca}_{9.5}\text{Dy}_{0.5}(\text{PO}_4)_6(\text{OH})_{1.5}\text{O}_{0.5}$ in ref. [1] and downscaled by 3%.

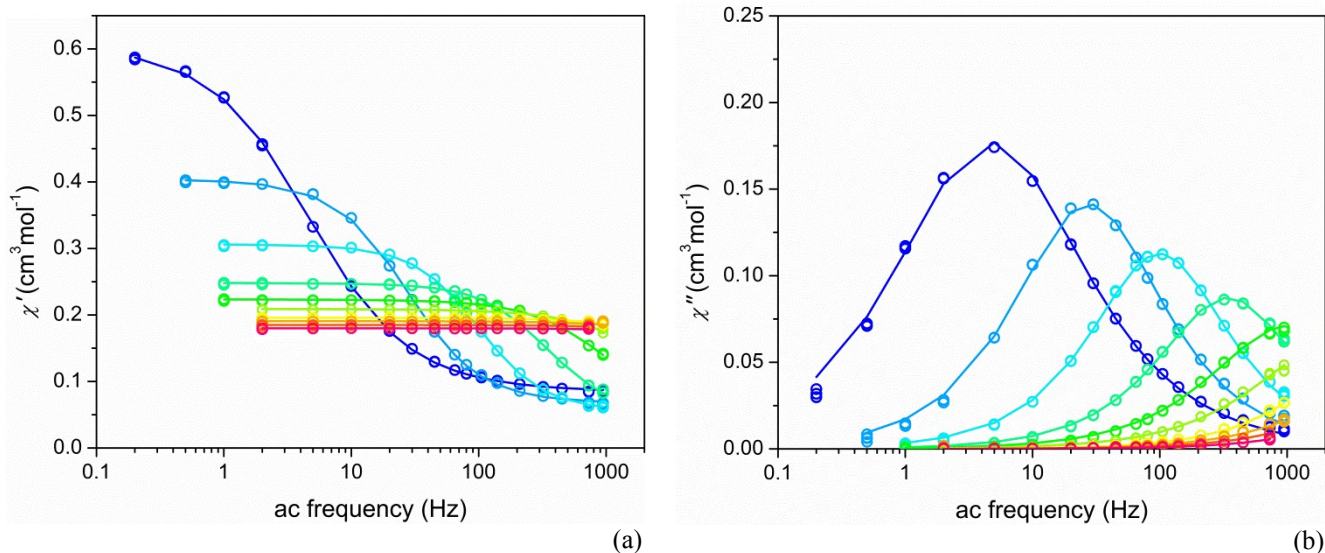


Figure S8. Frequency (f) dependence of ac susceptibility per mol of Dy under a zero magnetic field for **1**. (a) – in-phase susceptibility χ' , (b) – out-of-phase susceptibility χ'' . Symbols – experimental points, lines – fitting. The measurement temperature color designation – from blue to carmine-red – 20, 30, 40, 50, 56, 60, 64, 66, 68, 70 K.

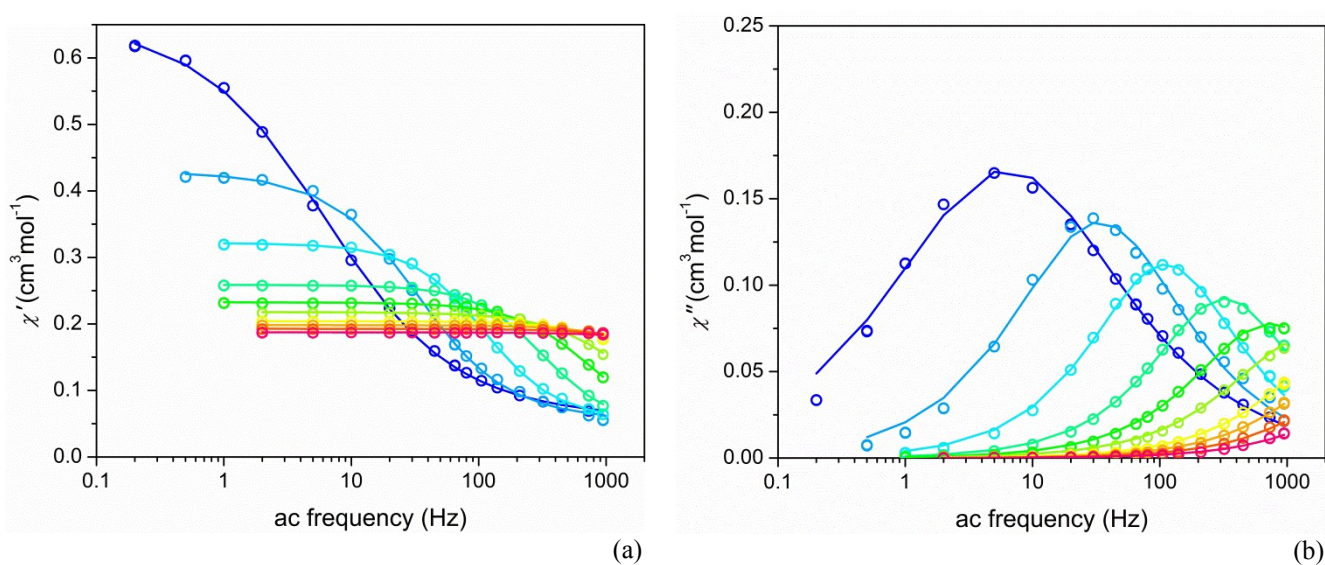


Figure S9. Frequency (f) dependence of ac susceptibility per mol of Dy under a zero magnetic field for **2**. (a) – in-phase susceptibility χ' , (b) – out-of-phase susceptibility χ'' . Symbols – experimental points, lines – fitting. The measurement temperature color designation – from blue to carmine-red – 20, 30, 40, 50, 56, 60, 64, 66, 68, 70 K.

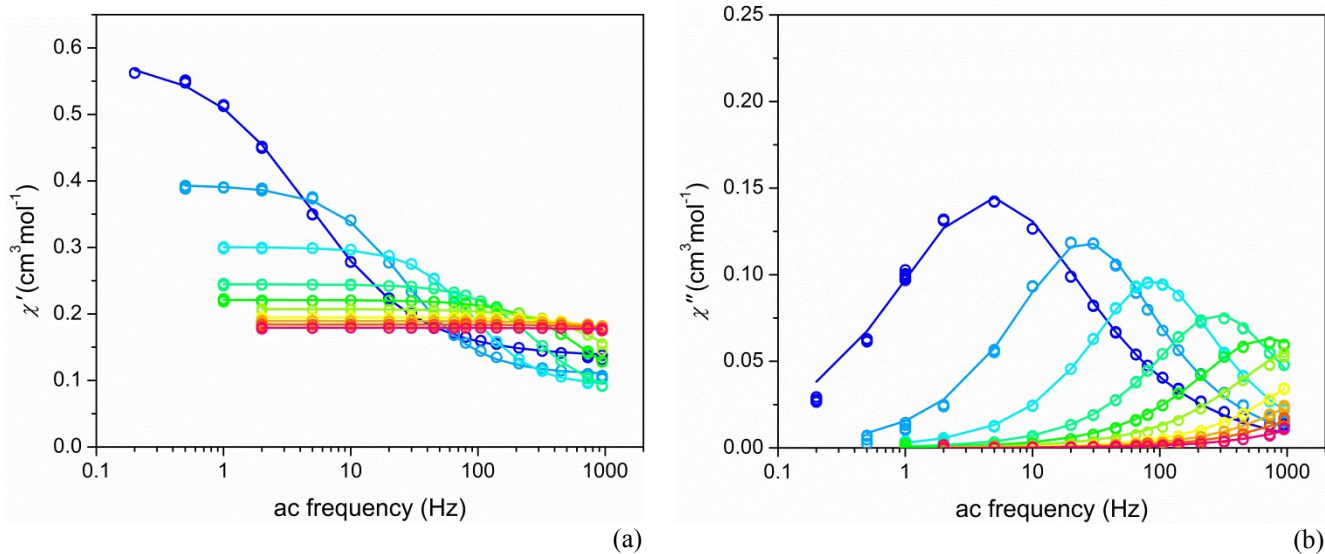


Figure S10. Frequency (f) dependence of ac susceptibility per mol of Dy under a zero magnetic field for **3**. (a) – in-phase susceptibility χ' , (b) – out-of-phase susceptibility χ'' . Symbols – experimental points, lines – fitting. The measurement temperature color designation – from blue to carmine-red – 20, 30, 40, 50, 56, 60, 64, 66, 68, 70 K.

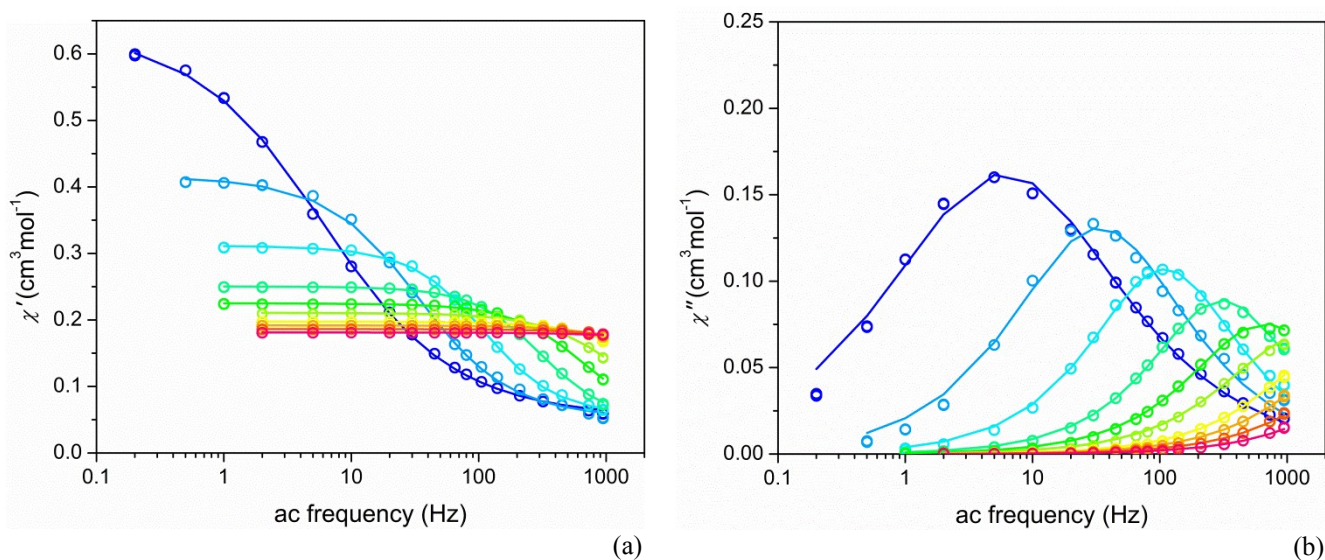


Figure S11. Frequency (f) dependence of ac susceptibility per mol of Dy under a zero magnetic field for **4**. (a) – in-phase susceptibility χ' , (b) – out-of-phase susceptibility χ'' . Symbols – experimental points, lines – fitting. The measurement temperature color designation – from blue to carmine-red – 20, 30, 40, 50, 56, 60, 64, 66, 68, 70 K.

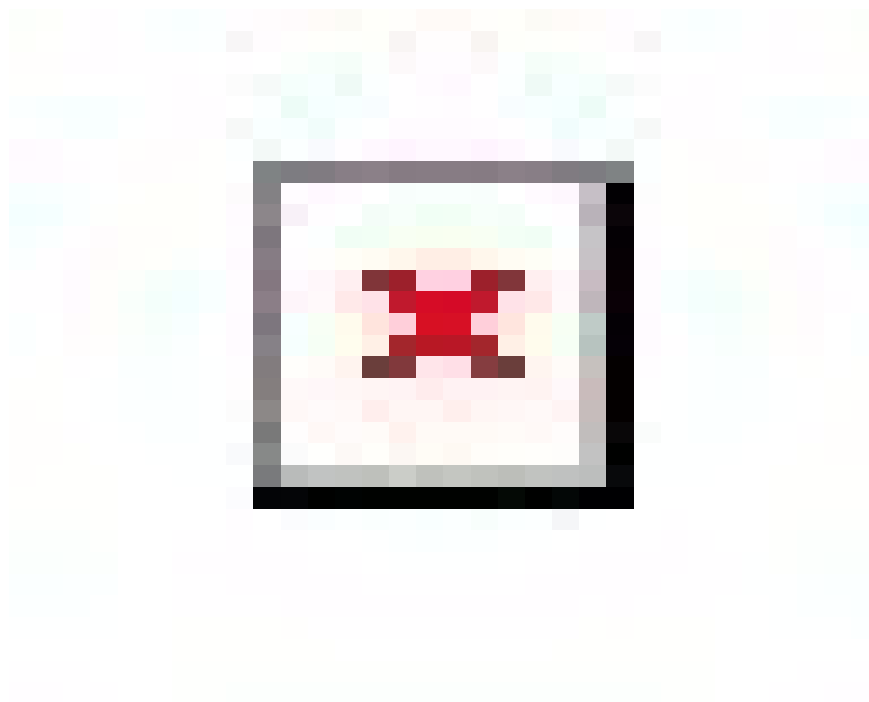


Figure S12. Field dependence of $\Delta M = M_{\text{down}} - M_{\text{up}}$ derived from hysteresis magnetization curves $M(H)$ at a temperature of 1.8 K and at a field sweeping rate of $50 \text{ Oe} \cdot \text{s}^{-1}$ for $\text{Ca}_{9.5}\text{Dy}_{0.5}(\text{PO}_4)_6(\text{OH})_{1.5}\text{O}_{0.5}$ (blue symbols) and $\text{Ca}_9\text{Dy}(\text{PO}_4)_6(\text{OH})\text{O}$ (red symbols), the compounds being reported in ref. [1] where designated as **1** and **2** respectively.

References

- 1 P. E. Kazin, M. A. Zykin, V. V. Utochnikova, O. V. Magdysyuk, A. V. Vasiliev, Y. V. Zubavichus, W. Schnelle, C. Felser and M. Jansen, *Angew. Chem. Int. Ed.* 2017, **129**, 13416.