# $Na_7[SbW_6O_{24}]$: a new type of turn-off luminescence humidity sensor based on a lanthanide-free polyoxometalate

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# Electronic Supporting Information

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**Fig. S1** Comparison between PXRD patterns of **$NaSbW_6 \cdot 10H_2O$** obtained (a) by thermally dehydrating **$NaSbW_6 \cdot 16H_2O$** at 50 °C overnight (blue line), and (b) by stirring the powder of **$NaSbW_6 \cdot 16H_2O$** in acetone overnight at room temperature (red line).

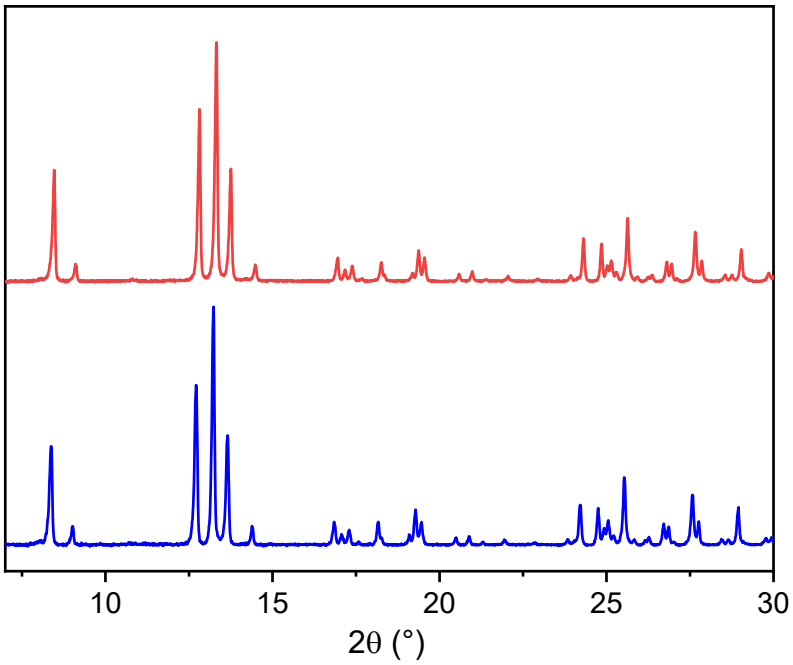


**Fig. S2** TGA (black line) and DSC (blue line) curves of **$NaSbW_6 \cdot 10H_2O$**.

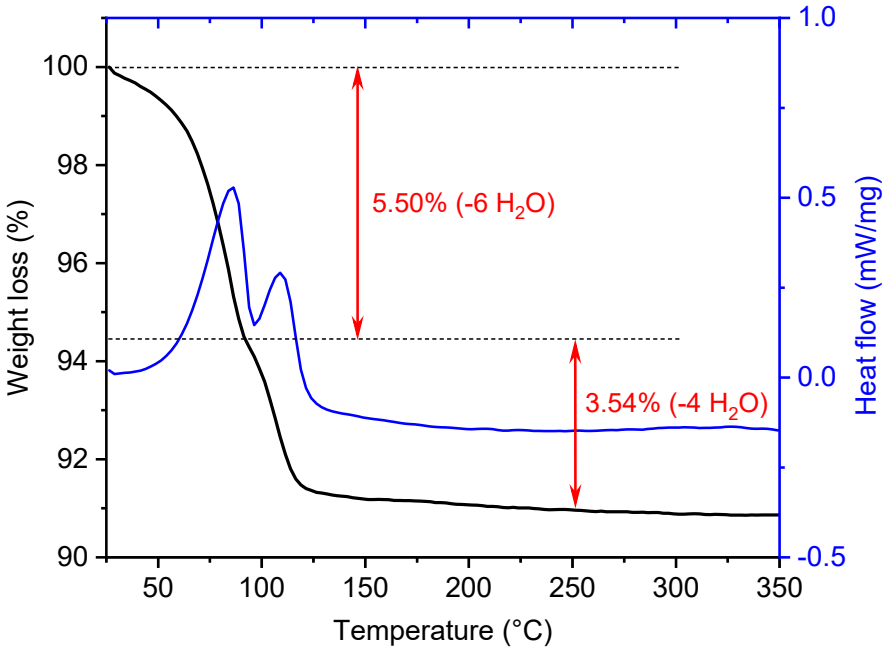


**Table S1** atom positions, site occupation fractions and atomic displacement parameters for **$NaSbW_6 \cdot 10H_2O$** at 30°C. a, b, and c stand for oxygen atoms linked by $C_{3i}$ symmetry. Atomic displacement parameters are constrained to be equal for each atom type.

| S.G. $P\bar{1}$, a(Å) = 7.3865(1), b(Å) = 10.2513(1), c(Å) = 11.3135(2), α(°) = 73.9061(11), β(°) = 71.5584(10), γ(°) = 76.483(1), $R_{Bragg}$ = 3.60, GOF = 1.31, $R_{wp}$ = 11.09 | | | | | | |
|---|---|---|---|---|---|---|
| atom | x | y | z | SOF | Wyckoff | $U_{iso}$ (Å$^2$) |
| Na1 | 0.217(3) | -0.697(2) | 0.2045(18) | 1 | 2i | 0.004(3) |
| Na2 | -0.405(3) | -0.430(2) | 0.578(2) | 1 | 2i | 0.004 |
| Na3 | 0.548(3) | -0.438(2) | 0.1176(18) | 1 | 2i | 0.004 |
| Na4 | 0 | 0 | 0.5 | 1 | 1b | 0.004 |
| Ow1 | 1.224(4) | 0.044(3) | 1.290(3) | 1 | 2i | 0.0263(15) |
| Ow2 | -0.245(4) | -0.554(3) | 0.397(3) | 1 | 2i | 0.0263 |
| Ow3 | 0.582(4) | -0.203(3) | -0.022(3) | 1 | 2i | 0.0263 |
| Ow4 | 0.079(5) | -0.610(4) | 0.397(3) | 1 | 2i | 0.0263 |
| Ow5 | 0.370(5) | -0.372(3) | 0.300(3) | 1 | 2i | 0.0263 |
| O1a | -0.164(3) | -0.167(3) | 0.0986(18) | 1 | 2i | 0.0263 |
| O1b | -0.048 | 0.295 | -0.2413 | 1 | 2i | 0.0263 |
| O1c | 0.262 | -0.479 | 0.0692 | 1 | 2i | 0.0263 |
| O2a | -0.146(3) | -0.443(3) | 0.1414(18) | 1 | 2i | 0.0263 |
| O2b | 0.221 | -0.174 | -0.041 | 1 | 2i | 0.0263 |
| O2c | -0.022 | 0.299 | 0.0996 | 1 | 2i | 0.0263 |
| O3a | 0.166(3) | -0.184(3) | -0.3724(18) | 1 | 2i | 0.0263 |
| O3b | 0.435 | -0.308 | -0.2285 | 1 | 2i | 0.0263 |
| O3c | 0.006 | 0.012 | -0.195 | 1 | 2i | 0.0263 |
| O4a | -0.365(3) | 0.024(3) | 0.283(2) | 1 | 2i | 0.0263 |
| O4b | 0.373 | 0.272 | -0.373 | 1 | 2i | 0.0263 |
| O4c | 0.115 | 0.159 | -0.439 | 1 | 2i | 0.0263 |
| W1 | 0.1790(4) | 0.1534(2) | -0.29748(16) | 1 | 2i | 0.0183(3) |
| W2 | -0.0382(4) | 0.3364(4) | -0.08062(16) | 1 | 2i | 0.0183 |
| W3 | -0.2197(4) | 0.1832(2) | 0.2165(2) | 1 | 2i | 0.0183 |
| Sb1 | 0 | 0 | 0 | -1 | 1a | 0.010(2) |

**Fig. S3** Top: Water molecules network around the $[SbW_6O_{24}]^{7-}$ unit in **$NaSbW_6 \cdot 16H_2O$**. Bottom: Structural similarities between **$NaSbW_6 \cdot 16H_2O$** (left), and **$NaSbW_6 \cdot 10H_2O$** (right) (grey octahedra: $WO_6$, pink octahedra: $SbO_6$, green octahedra: $NaO_6$, orange spheres: oxygen of $[SbW_6O_{24}]^{7-}$, blue sphere: oxygen of water molecules. H-bonding interactions are displayed as blue dotted lines between oxygen atoms.

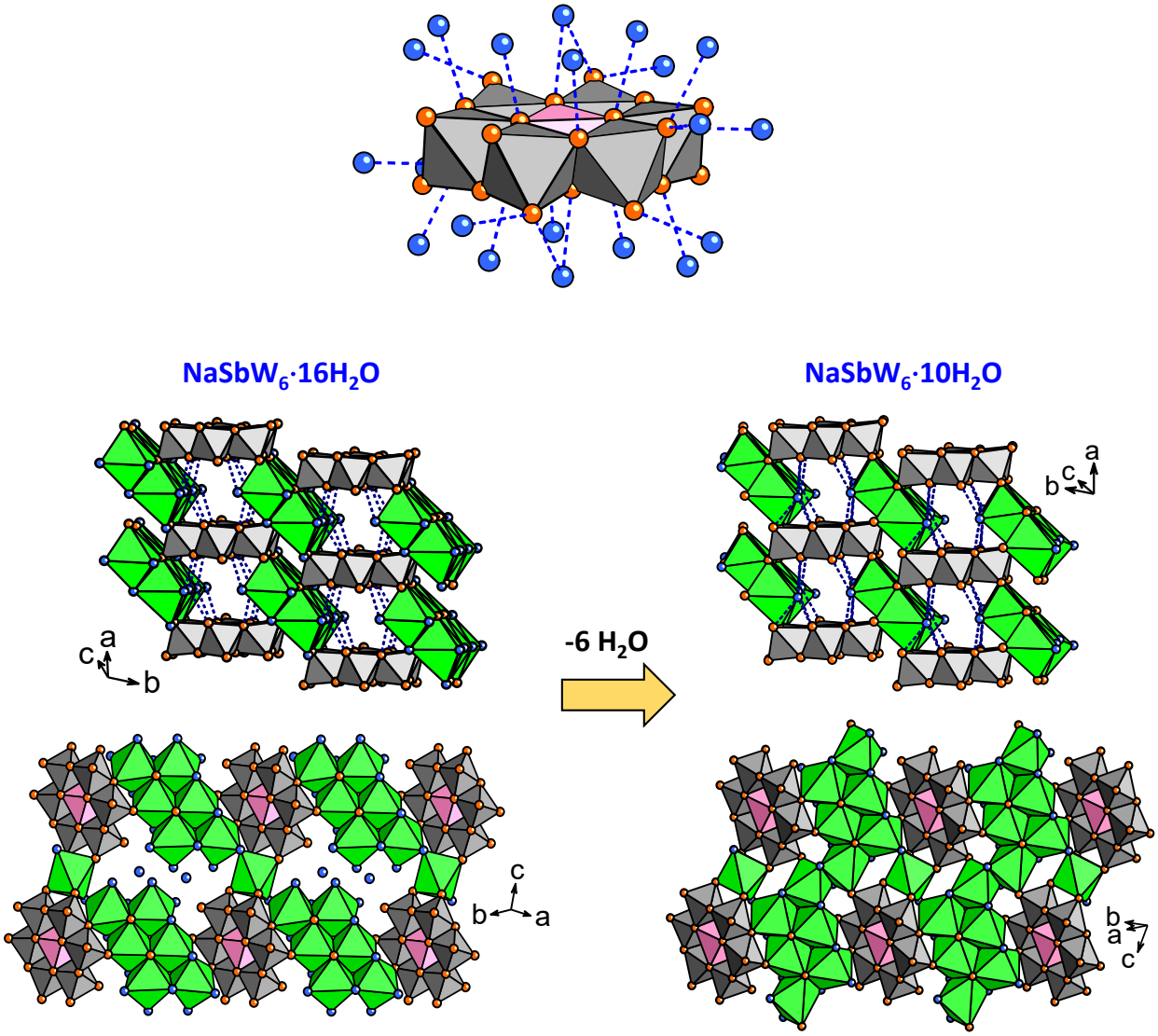


**Fig. S4** Comparison between PXRD patterns of **$NaSbW_6 \cdot 16H_2O$** exposed at 0%-5% RH for 4h (black line), **$NaSbW_6$** (red line), and **$NaSbW_6 \cdot 4H_2O$** (blue line).

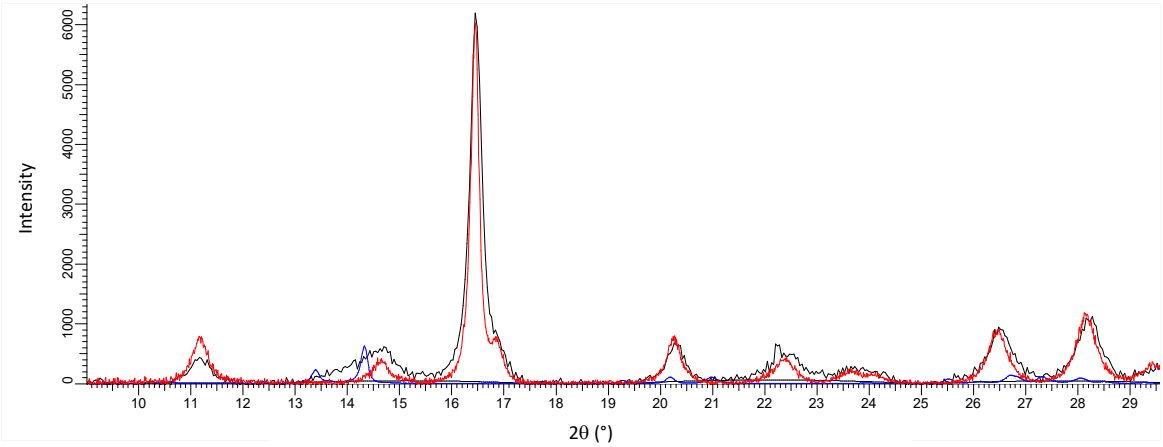


**Fig. S5** Room-temperature absorption spectra of **$NaSbW_6 \cdot 16H_2O$**, **$NaSbW_6 \cdot 10H_2O$**, **$NaSbW_6 \cdot 4H_2O$**, and **$NaSbW_6$**.

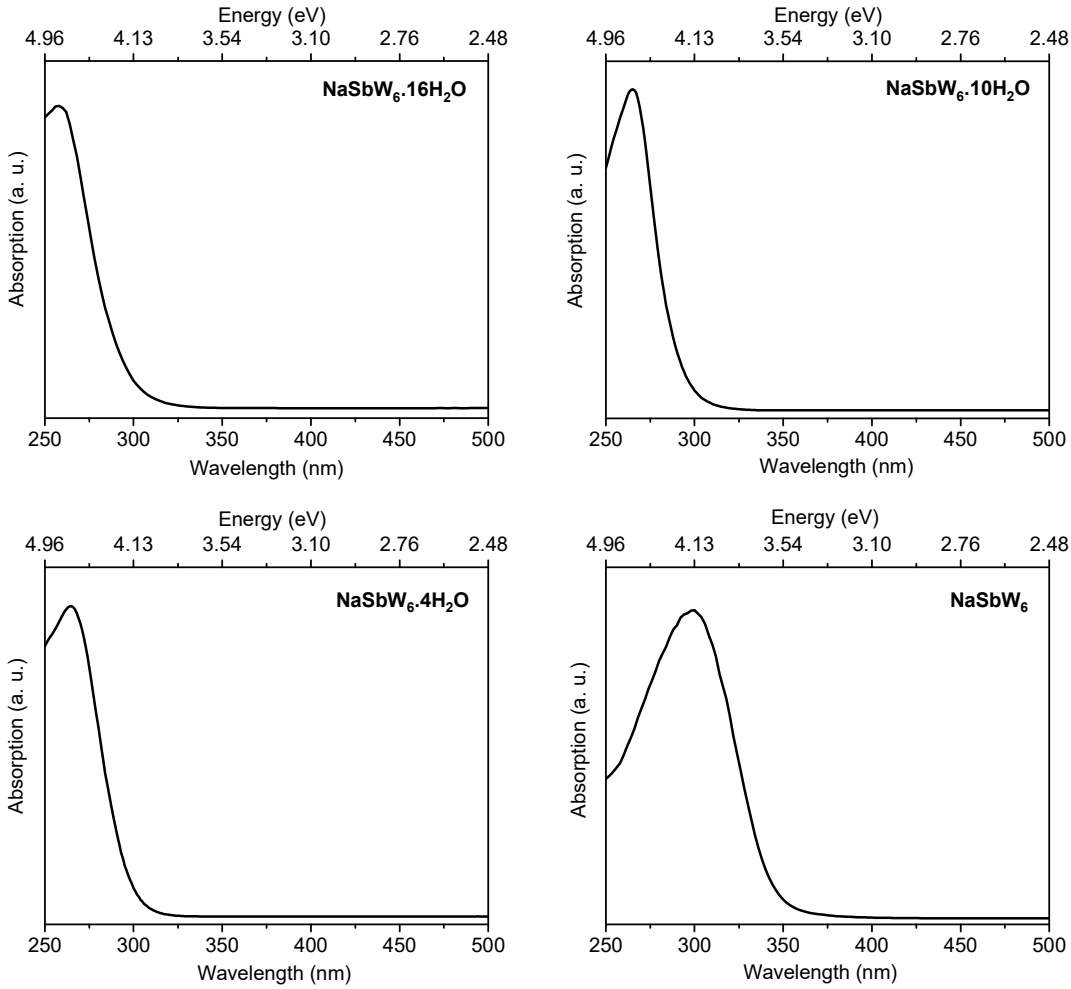
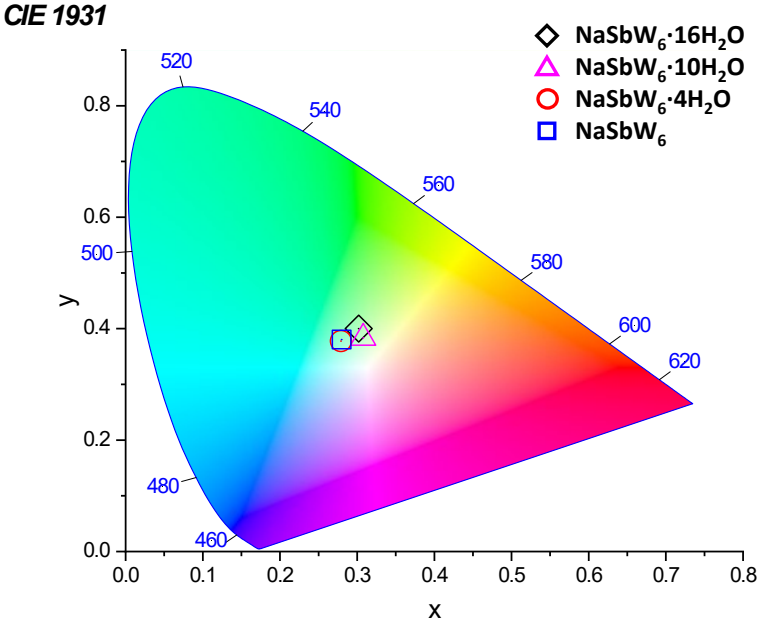


**Fig. S6** CIE chromaticity diagrams and chromaticity coordinates of **$NaSbW_6 \cdot 10H_2O$**, and **$NaSbW_6 \cdot 4H_2O$**, compared with those previously reported for **$NaSbW_6 \cdot 16H_2O$**, and **$NaSbW_6$**.




| Composé | x | y |
|---|---|---|
| **$NaSbW_6 \cdot 16H_2O$** | 0.30189 | 0.40019 |
| **$NaSbW_6 \cdot 10H_2O$** | 0.30779 | 0.38333 |
| **$NaSbW_6 \cdot 4H_2O$** | 0.27912 | 0.37776 |
| **$NaSbW_6$** | 0.27997 | 0.38042 |

**Fig. S7** Room-temperature photoluminescence decay curves ($\lambda_{ex}$ = 254 nm) monitored at 513 nm for **$NaSbW_6 \cdot 10H_2O$** (■), and **$NaSbW_6 \cdot 4H_2O$** (●). The I = f(*t*) plots have been properly fitted by a monoexponential law (red lines). Extracted decay times (τ) and regression coefficients ($R^2$) are indicated.

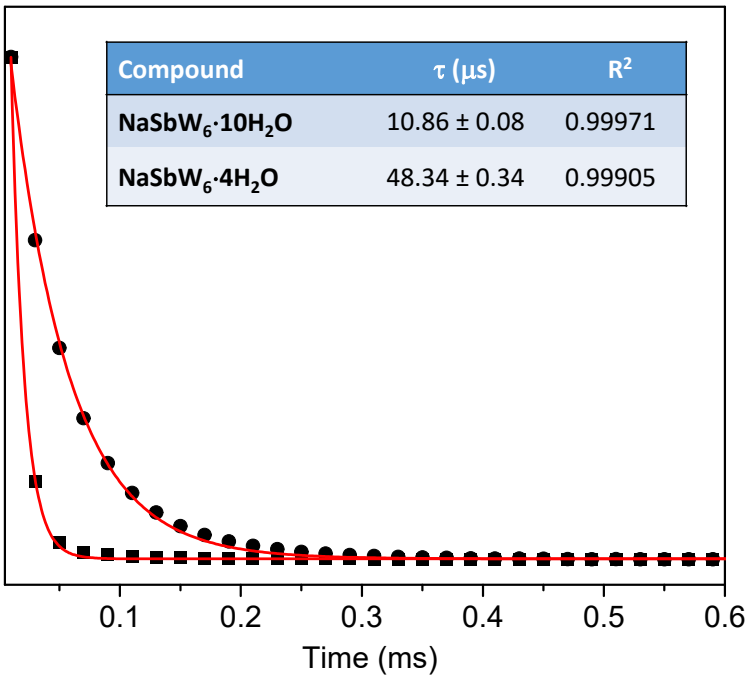


**Fig. S8** Room-temperature PL spectra (recorded upon excitation at 254 nm) of **$NaSbW_6$** at different RH levels compared with that of the **$NaSbW_6 \cdot 16H_2O$** reference.

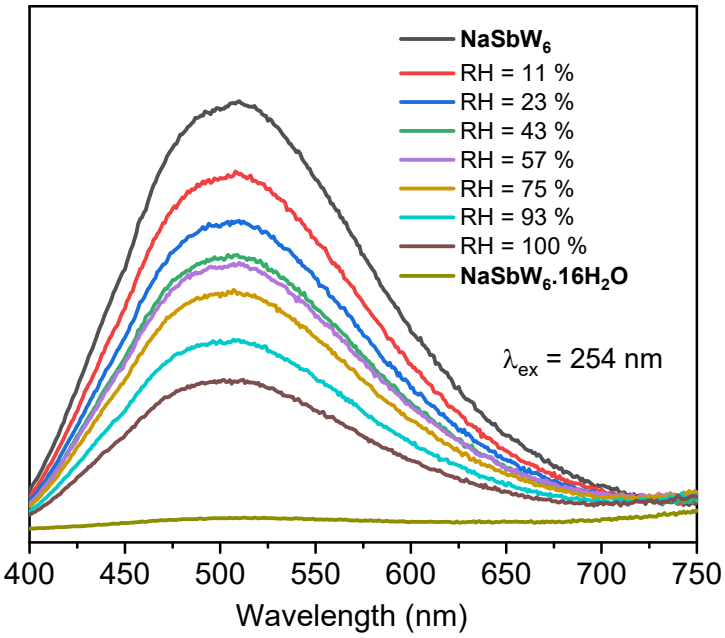


**Table S2** Crystallographic data of **$NaSbW_6 \cdot 16H_2O$**, **$NaSbW_6 \cdot 10H_2O$**, and **$NaSbW_6$**.

| Compound | **$NaSbW_6 \cdot 16H_2O$**[S1] | **$NaSbW_6 \cdot 10H_2O$** | **$NaSbW_6$** |
|---|---|---|---|
| Formula | $Na_7SbW_6O_{40}H_{32}$ | $Na_7SbW_6O_{34}H_{10}$ | $Na_7SbW_6O_{24}$ |
| M [g·mol$^{-1}$] | 2058 | 1951 | 1770 |
| Crystal system | triclinic | triclinic | trigonal |
| Space group | *P*-1 | *P*-1 | *R*-3 |
| a [Å] | 8.6026(5) | 7.3865(1) | 10.53600(18) |
| b [Å] | 10.1939(6) | 10.2513(1) | 10.53600(18) |
| c [Å] | 11.4666(5) | 11.3135(2) | 16.1942(5) |
| $\alpha$ [°] | 106.096(4) | 73.9061(11) | 90 |
| $\beta$ [°] | 91.180(4) | 71.5584(10) | 90 |
| $\gamma$ [°] | 107.231(5) | 76.483(1) | 120 |
| V [Å$^3$] | 916.97(9) | 770.75(2) | 1556.84(6) |
| *Z* | 1 | 1 | 3 |
| $\rho_{calcd}$ [g/cm$^3$] | 3.727 | 4.203 | 5.663 |
| T [K] | 130.15 | 293.15 | 303.15 |

## Reference

S1 A. A. Mukhacheva, M. R. Ryzhikov, T. Asanova, T. S. Sukhikh, N. B. Kompankov, V. V. Yanshole, A. S. Berezin, A. L. Gushchin, P. A. Abramov and M. N. Sokolov, *Curr. Inorg. Chem.*, 2017, **7**, 4–7.