

Supporting Information

BaWO₂F₄: A Mixed Anion X-ray Scintillator with Excellent Photoluminescence Quantum Efficiency

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Experimental section

Reagents

Ba(CH₃COO)₂ (Alfa Aesar, 99%), WO₃ (Sigma Aldrich, 99%), HCl (Sigma Aldrich, 37%), and HF (EMD, 49%) were used as received.

Warning! HF should only be handled in a well ventilated space and proper safety precautions must be used. If contact with the liquid or vapor occurs, proper treatment procedures should immediately be followed.

Synthesis

Single crystals of the titled compound, BaWO₂F₄, were grown by a mild hydrothermal synthetic route. Ba(CH₃COO)₂ (1 mmol), WO₃ (1 mmol), 0.5 ml of HCl and 1 ml of HF were added into a 23 ml PTFE liner. The PTFE liner was then placed in to stainless steel autoclave which was sealed, heated to 160 °C at a rate of 5 °C min⁻¹, held at this temperature for 24 hours, and cooled to room temperature at a rate of 6 °C h⁻¹. The mother liquor was decanted from the single crystal products, which were further isolated by filtration and washed with water and acetone. This reaction lead to a mixed phase product consisting of colorless rod crystals along with few powder of BaClF as an impurity. The impurity was removed by sonication in acetone followed by the decantation process.

Characterization

Single Crystal X-ray diffraction

Crystals formed as large stubby colorless rods. As-grown, uncleaved crystals gave very broad diffraction peaks with multiple maxima and strong diffuse streaking between Bragg spots. Several crystals were examined. Eventually a small platelike shard of dimensions 0.01 x 0.02 x 0.04 was used for data collection. X-ray intensity data were collected at 301(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$).¹ The data collection covered 99.5% of reciprocal space to $2\theta_{\text{max}} = 67.5^\circ$, with an average reflection redundancy of 7.4 and $R_{\text{int}} = 0.043$ after absorption

correction. The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.^{1,2} Final unit cell parameters were determined by least-squares refinement of 9875 reflections taken from the data set. An initial structural model was obtained with SHELXT.^{3a} Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018^{3b} using the ShelXle interface.⁴

The compound crystallizes in the monoclinic system. The space groups Pn and $P2/n$ were consistent with the pattern of systematic absences in the intensity data. The centrosymmetric space group $P2/n$ was confirmed by structure solution. The asymmetric unit consists of two tungsten atoms, two barium atoms, eight fluorine atoms and four oxygen atoms. All atoms are all located on positions of general crystallographic symmetry (site $4g$). All atoms were refined with anisotropic displacement parameters. A minor contribution from a twin domain related by pseudo-merohedry was identified in the latter refinement stages. This was suggested from the relatively low $R(\text{int})$ value of 0.31 for a C -centered orthorhombic cell ($a = 19.43 \text{ \AA}$, $b = 20.41 \text{ \AA}$, $c = 5.03 \text{ \AA}$, $V = 1995 \text{ \AA}^3$) output by XPREP. Such twinning is not uncommon in monoclinic crystal with $a \sim c$. The derived twin law is $(0\ 0\ -1 / 0\ -1\ 0 / -1\ 0\ 0)$, a two-fold axis parallel to the crystallographic $[-101]$ direction, exchanging the monoclinic a and c axes. Including twinning in the refinement lowered the final residuals from $R1/wR2 = 0.036/0.085$ to $0.030/0.069$ and improved the residual electron density from $+7.61 / -3.49$ to $+6.65 / -2.91 \text{ e}^-/\text{\AA}^3$. The minor twin domain fraction refined to $0.0174(4)$. The largest residual electron density peak and hole in the final difference map are both located $< 0.7 \text{ \AA}$ W1.

The crystallographic characteristics and results of the diffraction experiments are summarized in Table 1.

Table 1. Crystallographic data for BaWO₂F₄

	BaWO₂F₄
Formula weight	429.19
Crystal system	Monoclinic
Space group, Z	<i>P2/n</i>
a, Å	14.0464(8)
b, Å	5.0318(3)
c, Å	14.1297(8)
β, deg	92.811(3)
V, Å ³	997.47(10)
ρ _{calcd} , g/cm ³	5.716
Radiation (λ, Å)	MoK _α (0.71073)
μ, mm ⁻¹	30.895
T, K	300(2)
Crystal dim., mm ³	0.010×0.020×0.040
2θ range, deg.	2.886 - 33.680
Reflections collected	32174
Data/restraints/parameters	3974/0/146
R _{int}	0.0432
Goodness of fit	1.092
R ₁ (I > 2σ(I))	0.0298
wR ₂ (all data)	0.0694

Powder X-ray Diffraction

Powder X-ray diffraction (PXRD) data for phase purity confirmation were collected on polycrystalline samples obtained by grinding single crystals. Data were collected on a Bruker D2 PHASER diffractometer utilizing Cu K_α radiation. The data were collected over the range from 10 to 80° in 2θ with a step size of 0.02°. Rietveld analysis pattern for XRD data of BaWO₂F₄, is shown in Figure S1.

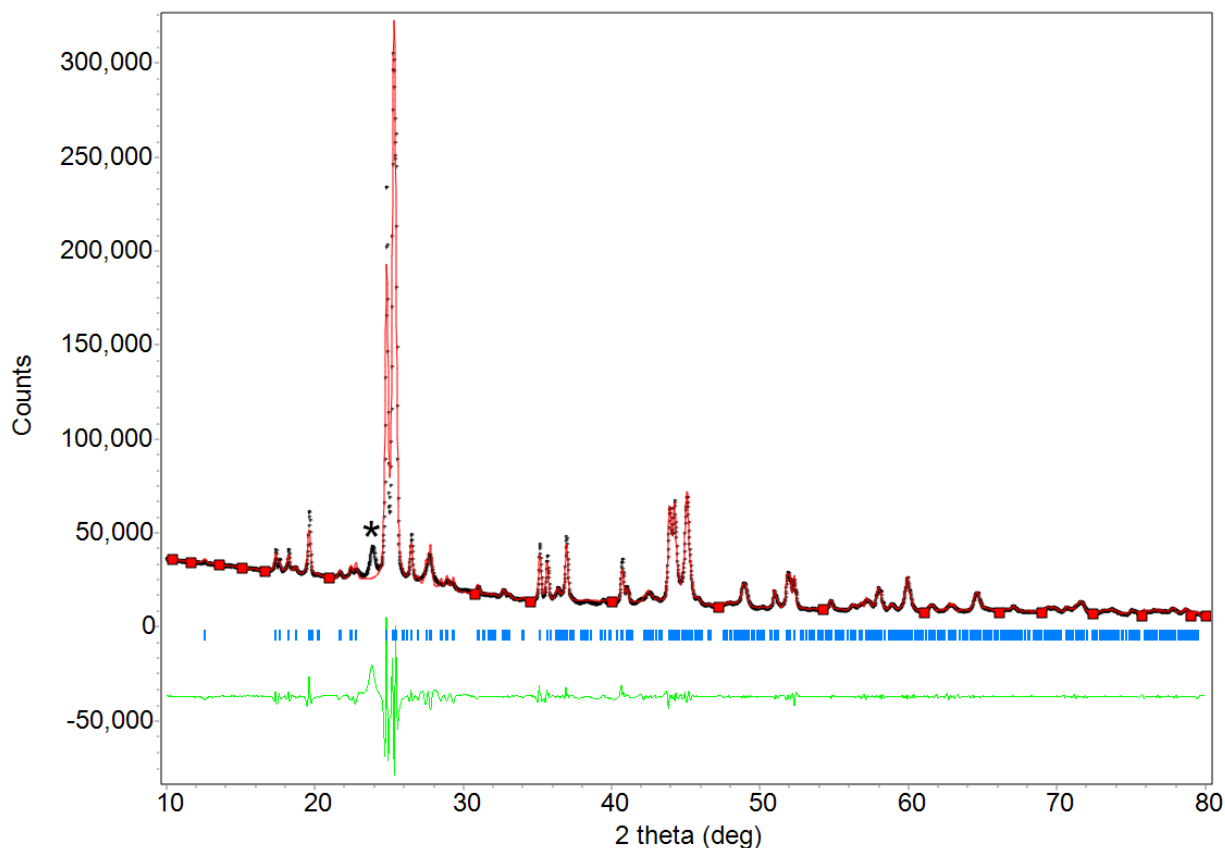


Figure S1. Whole pattern fitting of the BaWO₂F₄ PXRD pattern using Le Bail method. The star (*) denotes an unidentified impurity. The solid black and red lines denote the observed and calculated pattern respectively. The short blue lines show the position of the Bragg reflections and the green solid lines are the difference between the observed and calculated intensities.

Energy-Dispersive Spectroscopy (EDS)

A scanning electron micrograph of a single crystal of BaWO₂F₄ was obtained using a Tescan Vega-3 SEM instrument equipped with a Thermo EDS attachment (Figure S2). The SEM was operated in low vacuum mode. The crystal was mounted on an SEM stub with carbon tape and analyzed using a 20 kV accelerating voltage and an 80 s accumulating time. The results of EDS confirm the presence of elements found by single-crystal X-ray diffraction (Table 2).

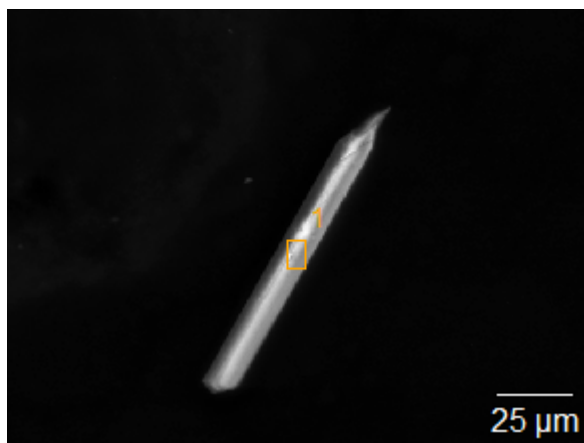


Figure S2. Single crystal SEM image of BaWO₂F₄

Table 2. EDS results

BaWO ₂ F ₄	
Element	Atom %
Ba	12.69
W	11.01
O	23.99
F	52.31

Optical properties

Fluorescence data was collected on ground samples of BaWO₂F₄ single crystals using a PerkinElmer LS55 luminescence spectrometer. Excitation spectra was collected at emission wavelength of 520 nm and emission scan was collected at excitation wavelength of 286 nm.

Scintillation image of BaWO₂F₄ was taken using a Rigaku Ultima IV diffractometer equipped with a Cu K α source ($\lambda = 1.54018 \text{ \AA}$).

Quantum yield measurements were collected on an Edinburgh Instruments FS5 fluorescence spectrometer using the SC-30 Integration Sphere Module, equipped with a 150 W Continuous Wave Xenon Lamp source for excitation. Solid samples were placed on a polytetrafluoroethylene (PTFE) solid-state sample holder that was loaded into the integration sphere.

All first-principles calculations are performed based on density functional theory (DFT) using the projector augmented wave (PAW) method as implemented in the Vienna *ab initio* simulation package (VASP). The Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA) is chosen as the exchange-correlation functional, and the kinetic energy cutoff of the wave functions is set as 600 eV. All geometries are fully optimized until the energy convergence threshold is smaller than 10^{-5} eV and the maximal Hellmann-Feynman force is smaller than 10^{-3} eV/Å.

The optimized atomic structure of BaWO_4 and BaWO_2F_4 is shown in Figure S3. After structure optimization, the W-W bond distance of BaWO_4 is 5.707 Å. For BaWO_2F_4 , the corresponding bond distance is extended to 6.520 Å which reduces the orbital overlap resulting in narrow bands that can stabilize the self-trapped excitons and promote strong exciton emission at room temperature.

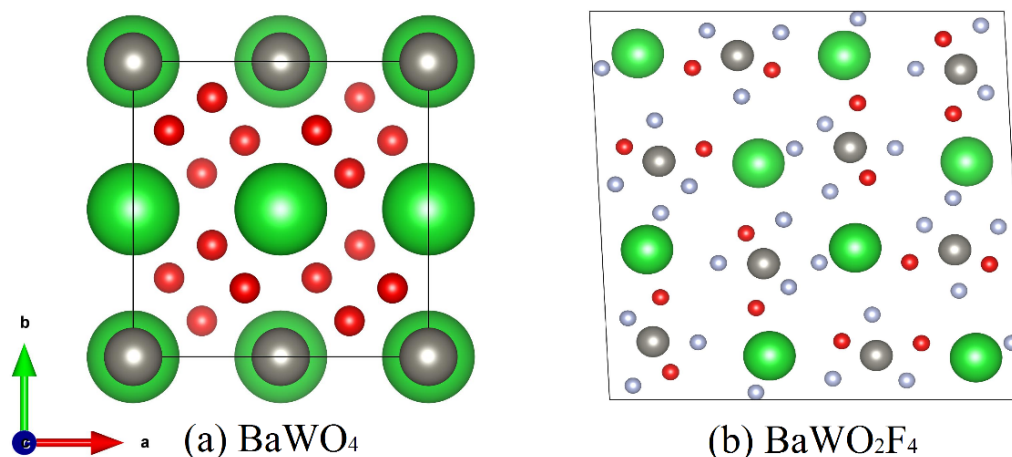


Figure S3. Optimized atomic structure of (a) BaWO_4 and (b) BaWO_2F_4 . Color coding: green, Ba; gray, W; light blue, F; red, O.

Thermal Analyses

Thermogravimetric analyses was performed using a PerkinElmer Pyris 1 TGA system by heating the sample at a rate of $10\text{ }^\circ\text{C}/\text{min}$ under flowing O_2 gas up to a temperature of $1200\text{ }^\circ\text{C}$. The thermal products were analyzed by PXRD.

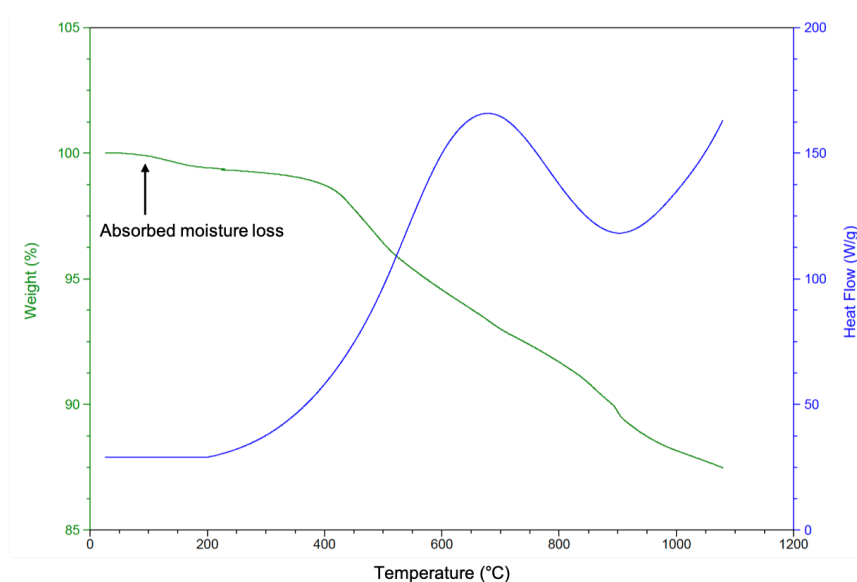


Figure S4. Thermogravimetric analysis diagram for BaWO_2F_4

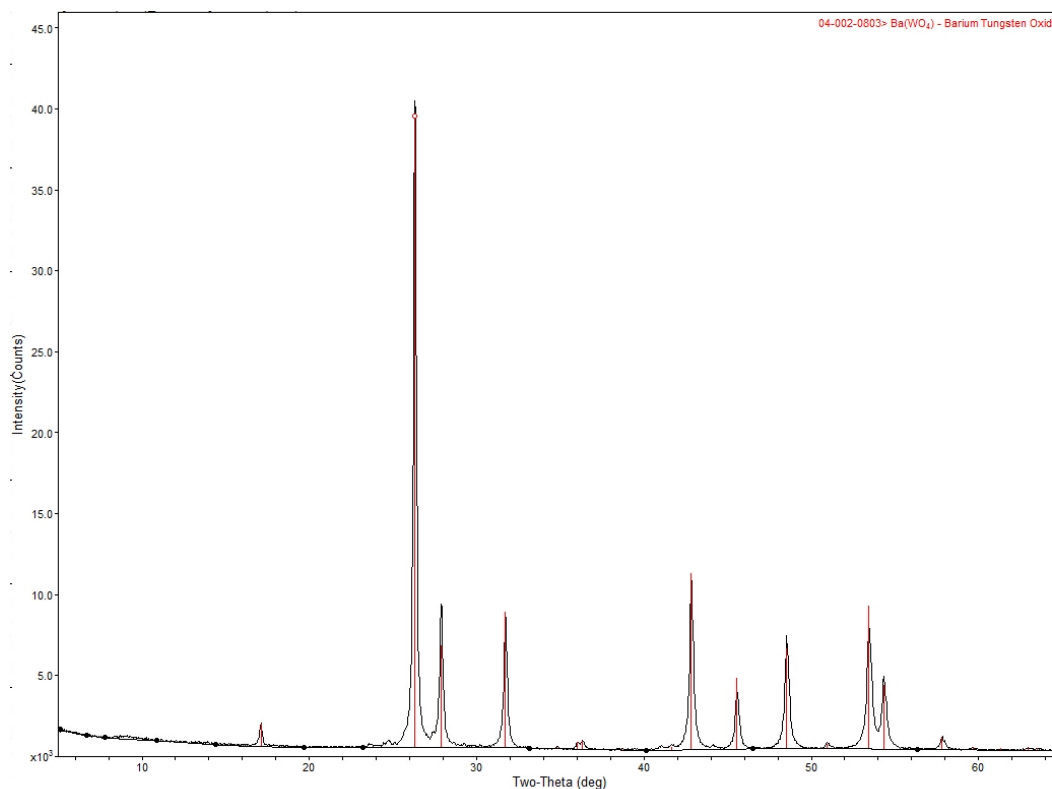


Figure S5. Powder X-ray diffraction pattern of the TGA residues after thermal decomposition of BaWO_2F_4 at 400 °C under oxygen gas flowing.

References

- (1) **APEX3** Version 2016.5-0 and **SAINT+** Version 8.37A. Bruker AXS, Inc., Madison, Wisconsin, USA, 2016.
- (2) **SADABS-2016/2**: Krause, L., Herbst-Irmer, R., Sheldrick G.M. and Stalke D. *J. Appl. Cryst.* **2015**, *48*, 3-10.
- (3) (a) **SHELXT**: Sheldrick, G.M. *Acta Cryst.* **2015**, *A71*, 3-8. (b) **SHELXL**: Sheldrick, G.M. *Acta Cryst.* **2015**, *C71*, 3-8.
- (4) **ShelXle**: a Qt graphical user interface for **SHELXL**. Hübschle, C. B., Sheldrick, G. M., Bittrich, B. *J. Appl. Cryst.* **2011**, *44*, 1281-1284.