Supporting Information

BaWO$_2$F$_4$: A Mixed Anion X-ray Scintillator with Excellent Photoluminescence Quantum Efficiency

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Experimental section

Reagents
Ba(CH\textsubscript{3}COO\textsubscript{2}) (Alfa Aesar, 99%), WO\textsubscript{3} (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, BaWO\textsubscript{2}F\textsubscript{4}, were grown by a mild hydrothermal synthetic route. Ba(CH\textsubscript{3}COO)\textsubscript{2} (1 mmol), WO\textsubscript{3} (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 into stainless steel autoclave which was sealed, heated to 160 °C at a rate of 5 °C min\textsuperscript{-1}, held at this temperature for 24 hours, and cooled to room temperature at a rate of 6 °C h\textsuperscript{-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 Ka radiation, λ = 0.71073 Å). \textsuperscript{1} The data collection covered 99.5% of reciprocal space to 2θ\textsubscript{max} = 67.5°, with an average reflection redundancy of 7.4 and R\textsubscript{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.\textsuperscript{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.\textsuperscript{3a} Subsequent difference Fourier calculations and full-matrix least-squares refinement against $F^2$ were performed with SHELXL-2018\textsuperscript{3b} using the ShelXle interface.\textsuperscript{4}

The compound crystallizes in the monoclinic system. The space groups $Pn$ and $P2/1n$ were consistent with the pattern of systematic absences in the intensity data. The centrosymmetric space group $P2/1n$ 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 $R$(int) value of of 0.31 for a $C$-centered orthorhombic cell ($a = 19.43$ Å, $b = 20.41$ Å, $c = 5.03$ Å, $V = 1995$ Å$^3$) 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 $+6.65 / -2.91$ e$^-$/Å$^3$. 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 Å W1.

The crystallographic characteristics and results of the diffraction experiments are summarized in Table 1.
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 Kα 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 BaWO$_2$F$_4$ 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 BaWO$_2$F$_4$ 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 BaWO$_2$F$_4$

Table 2. EDS results

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>12.69</td>
</tr>
<tr>
<td>W</td>
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</tr>
<tr>
<td>O</td>
<td>23.99</td>
</tr>
<tr>
<td>F</td>
<td>52.31</td>
</tr>
</tbody>
</table>

Optical properties

Fluorescence data was collected on ground samples of BaWO$_2$F$_4$ 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 BaWO$_2$F$_4$ was taken using a Rigaku Ultima IV diffractometer equipped with a Cu Kα source (λ = 1.54018 Å).
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$_2$F$_4$ is shown in Figure S3. After structure optimization, the W-W bond distance of BaWO$_4$ is 5.707 Å. For BaWO$_2$F$_4$, 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$_2$F$_4$. 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 °C/min under flowing O$_2$ gas up to a temperature of 1200 °C. The thermal products were analyzed by PXRD.

Figure S4. Thermogravimetric analysis diagram for BaWO$_2$F$_4$
Figure S5. Powder X-ray diffraction pattern of the TGA residues after thermal decomposition of BaWO$_2$F$_4$ at 400 °C under oxygen gas flowing.

References