

Lanthanide Thioborates, an Emerging Class of Nonlinear Optical Materials, Efficiently Synthesized Using the Boron-Chalcogen Mixture Method

Logan Breton¹, Gregory Morrison¹, Matthew Lacroix², P. Shiv Halasyamani², and Hans-Conrad zur Loye*¹

¹Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, SC, United States

*e-mail: zurloye@mailbox.sc.edu

²Department of Chemistry, University of Houston, Houston, TX, United States

Table of Contents

1. List of reagent identities, manufacturers, and purities	S2
2. Instruments and parameters	S3-S4
3. Phase pure LaBS ₃ PXRD	S5
4. SEM Images	S6
5. SEM Spectra	S7-S8
6. Elemental Compositions	S9
7. Fluorescence spectra for LnBS ₃ (Ln = Ce, Pr, Nd)	S10-S12
8. BaB ₂ S ₄ Synthesis Details	S13
9. Phase pure BaB ₂ S ₄ PXRD	S14
10. Image of obtained single crystals of BaB ₂ S ₄	S15
11. LaBS ₃ Tauc Plot	S16
12. SI References	S17

1. List of reagent identities, manufacturers, and purities

La₂O₃ (99.9%, Alfa Aesar), CeO₂ (99.9%, Alfa Aesar), Nd₂O₃ (99.9%, Acros Organics) CsI (99%, Strem Chemicals), NaI (certified/crystalline, Fisher Chemical), elemental boron (99.5%, Cerac), elemental sulfur (sublimed, Fischer Chemicals) and MeOH ($\geq 99.8\%$, Sigma-Aldrich). Pr₂O₃ was prepared by placing an alumina boat filled with Pr₆O₁₁ powder (99.99%, Alfa Aesar) into a tube furnace set to 1000 °C under a stream of hydrogen gas (5% Hydrogen-95% Nitrogen, Airgas) overnight. La₂O₃, CeO₂, and Nd₂O₃ were heat treated to remove hydroxide and carbonate impurities for the experiments by firing the powders at 1000 °C overnight. It is important to note that the presence of rare earth hydroxides will lead to the formation of an LnS₂ impurity, interfering with the formation of the orthothioborate. K₂S was prepared as stated in the literature.¹ The CsI-NaI eutectic flux and K₂S were stored in a nitrogen filled glovebag.

2. Instruments and parameters

Single Crystal X-ray Diffraction (SXR)

X-ray intensity data from single crystals of all title compounds were all collected at 300 K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$). The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.^{2,3} Final unit cell parameters were determined by least-squares refinement of large sets of reflections taken from each data set. An initial structural model was obtained with SHELXT.⁴ Subsequent difference Fourier calculations and full-matrix least-squares refinement against F² were performed with SHELXL-2018 using the Olex2 interface.^{5,6}

Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction data of LaBS₃ and BaB₂S₄ were collected on ground single crystalline samples of the products obtained. Data was collected on a Bruker D2 PHASER diffractometer using Cu K α radiation over a 2 θ range 10–65° with a step size of 0.02°.

Energy-dispersive spectroscopy (EDS)

EDS was performed on single crystals of the title compounds using a Tescan Vega-3 SEM equipped with a Thermo EDS attachment. The SEM was operated in low-vacuum mode. Crystals were mounted on an SEM stub with carbon tape and analyzed using a 20 kV accelerating voltage and an 80 s accumulation time.

Fluorescence Measurements

Fluorescence data were collected on HORIBA Scientific Standard Microscope Spectroscopy Systems connected with iHR320 Spectrometer and Synchrony detector operating on Labspec 6 software. Spectra were recorded from 400 to 800 nm using 375 nm laser excitation source power 0.5 mW with 10 \times UV objective.

UV-Vis Measurements

UV-vis spectra were recorded in the diffuse reflectance mode using a PerkinElmer Lambda 35 UV/visible scanning spectrophotometer equipped with an integrating sphere. Diffuse reflectance spectra were recorded in the 200–900 nm range. Reflectance data were converted to absorbance by the instrument via the Kubelka–Munk function.⁷ All optical measurements were performed on polycrystalline powders obtained by grinding the product single crystals.

Powder SHG Phase Matching Measurement

The SHG samples were prepared by grinding the as received sample of LaBS₃ with a mortar and pestle. The solid was sieved using 20, 45, 63, 75, 90, 125, and 150 μm sieves resulting in samples with particle size distributions of < 20, 20-45, 45-63, 63-75, 75-90, 90-125, and 125-150 μm. The samples were loaded into 1mm thick fused silica tubes and irradiated by a Nd:YAG laser (1064 nm fundamental radiation). The second-harmonic generated radiation at 532 nm was passed through a photomultiplier tube (PMT) and measured using an oscilloscope. For each sample the minimum value was extracted (the output signal is negative) and multiplied by a -1 to return a positive value and then plotted. Two reference materials, α-SiO₂ (non-phase-matchable under 1064 nm incident radiation) and KH₂PO₄ (phase-matchable under 1064 nm incident) were used. LaBS₃ is non-phase-matchable under 1064 nm incident radiation. As a result, α-SiO₂ was selected as the reference material.

3. Phase Pure LaBS₃ PXRD

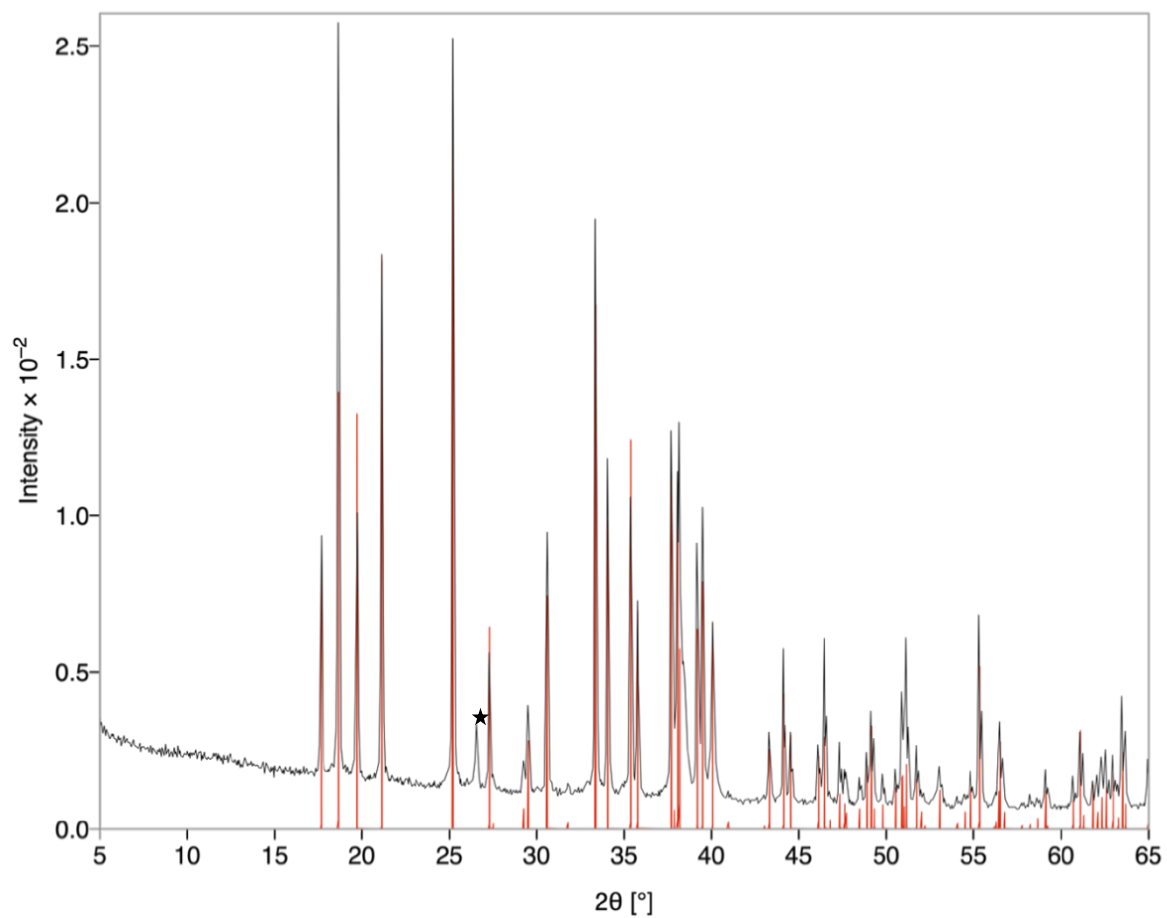


Figure S1. Powder X-ray Diffraction Pattern of the obtained phase pure sample of LaBS₃. A minor carbon impurity peak is denoted by a star.

4. SEM Images

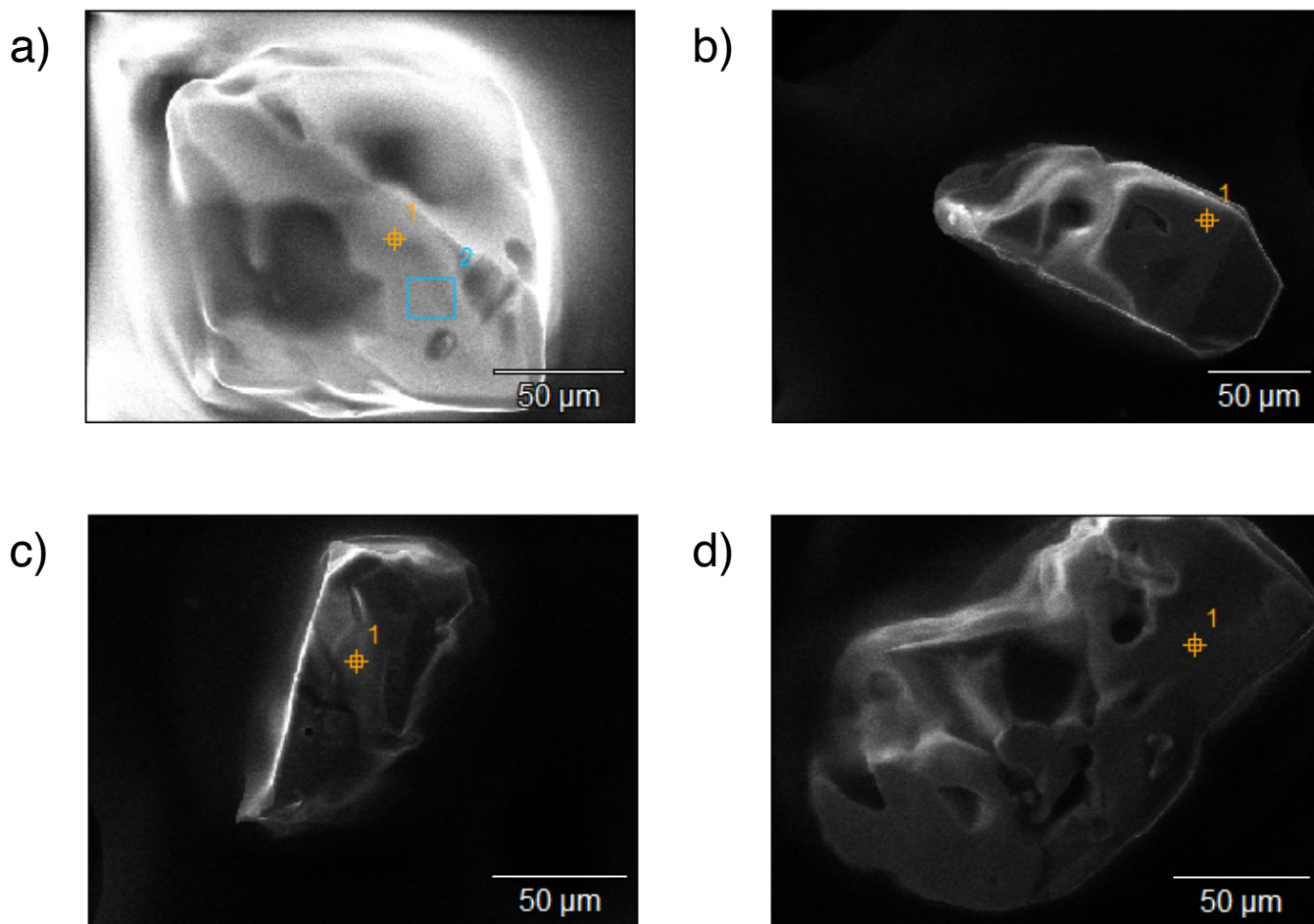


Figure S2. SEM images of (a) LaBS_3 , (b) CeBS_3 , (c) PrBS_3 , and (d) NdBS_3 .

5. SEM Spectra

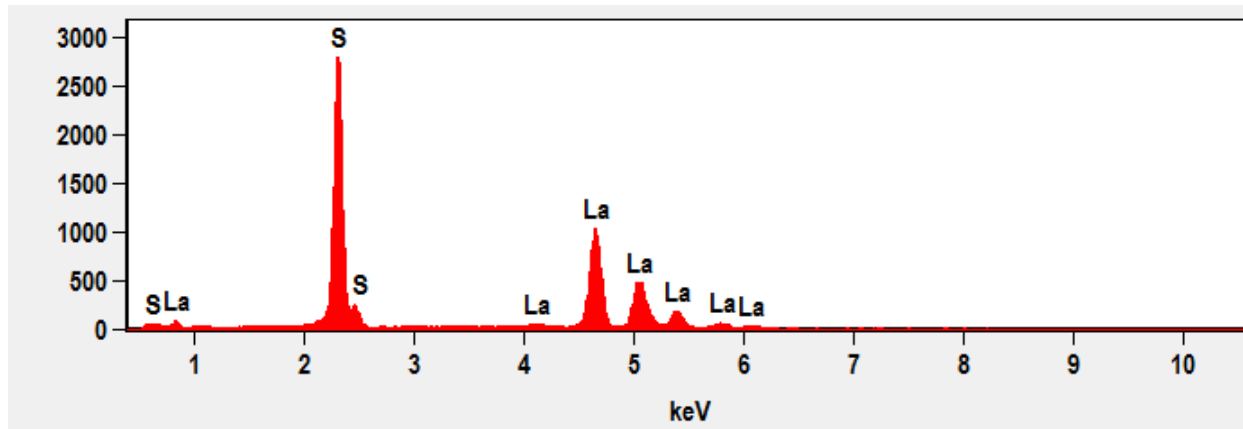


Figure S3. EDS spectrum of LaBS₃.

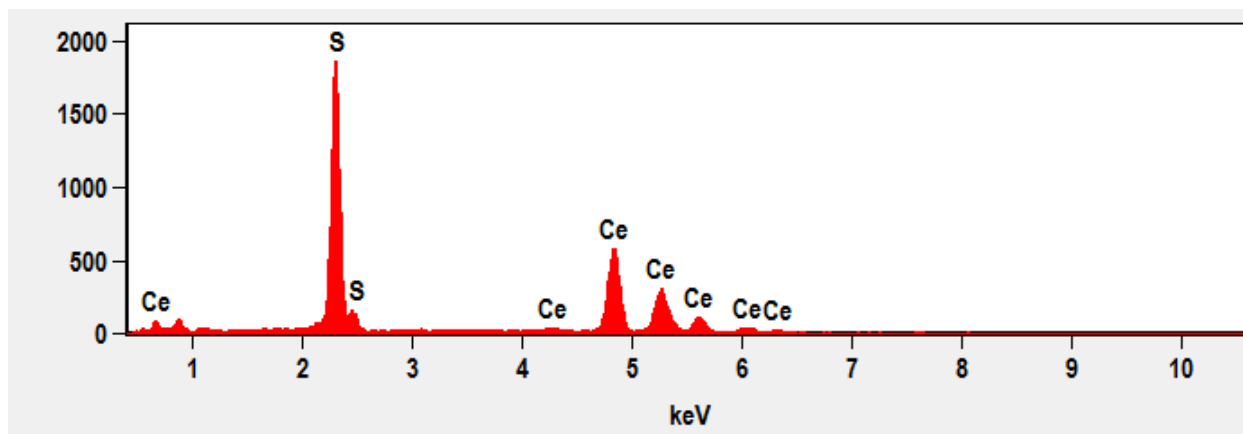


Figure S4. EDS spectrum of CeBS₃.

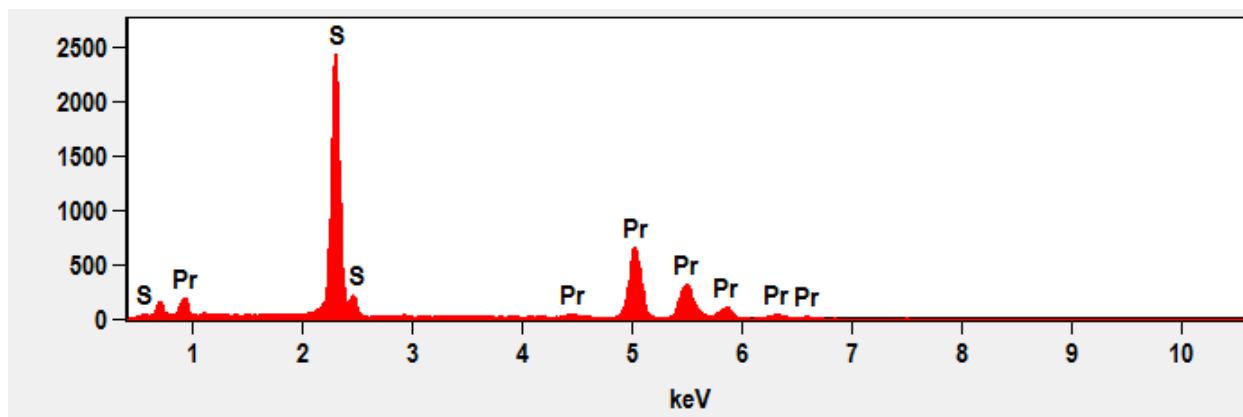


Figure S5. EDS spectrum for PrBS₃.

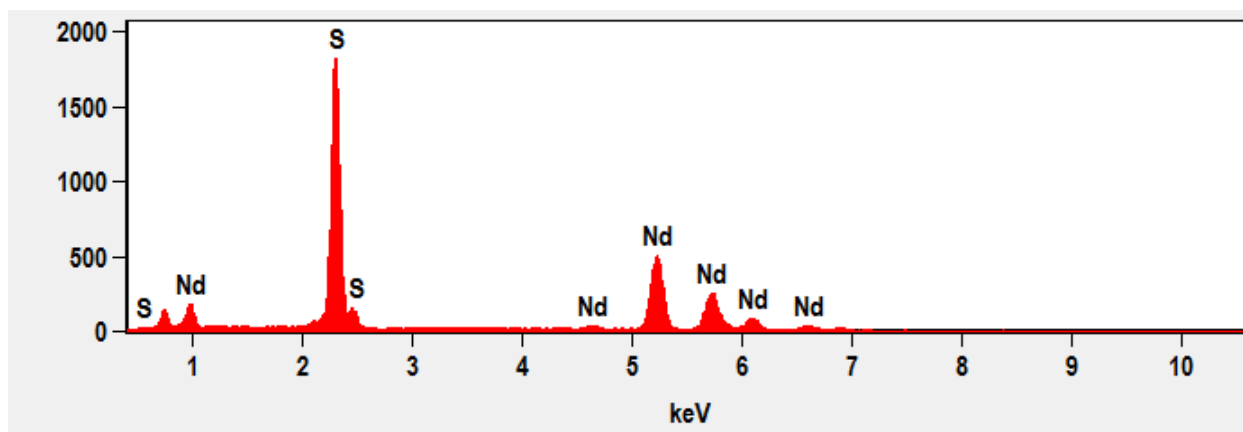


Figure S6. EDS spectrum of NdBS₃.

6. Elemental Compositions

Table S1. Elemental compositions of the rare earth thioborates as determined by EDS.

LaBS ₃		CeBS ₃		PrBS ₃		NdBS ₃	
Element	Atom%	Element	Atom%	Element	Atom%	Element	Atom%
La	23.71	Ce	21.77	Pr	19.78	Nd	20.11
S	76.29	S	78.23	S	80.22	S	79.89

7. Fluorescence Data

Fluorescence spectra were obtained at an excitation wavelength of 375 nm on single crystals of all title compounds, Figures S7-9. No fluorescence from LaBS₃ was observed, as expected, due to lanthanum's 4f⁰ electron configuration.

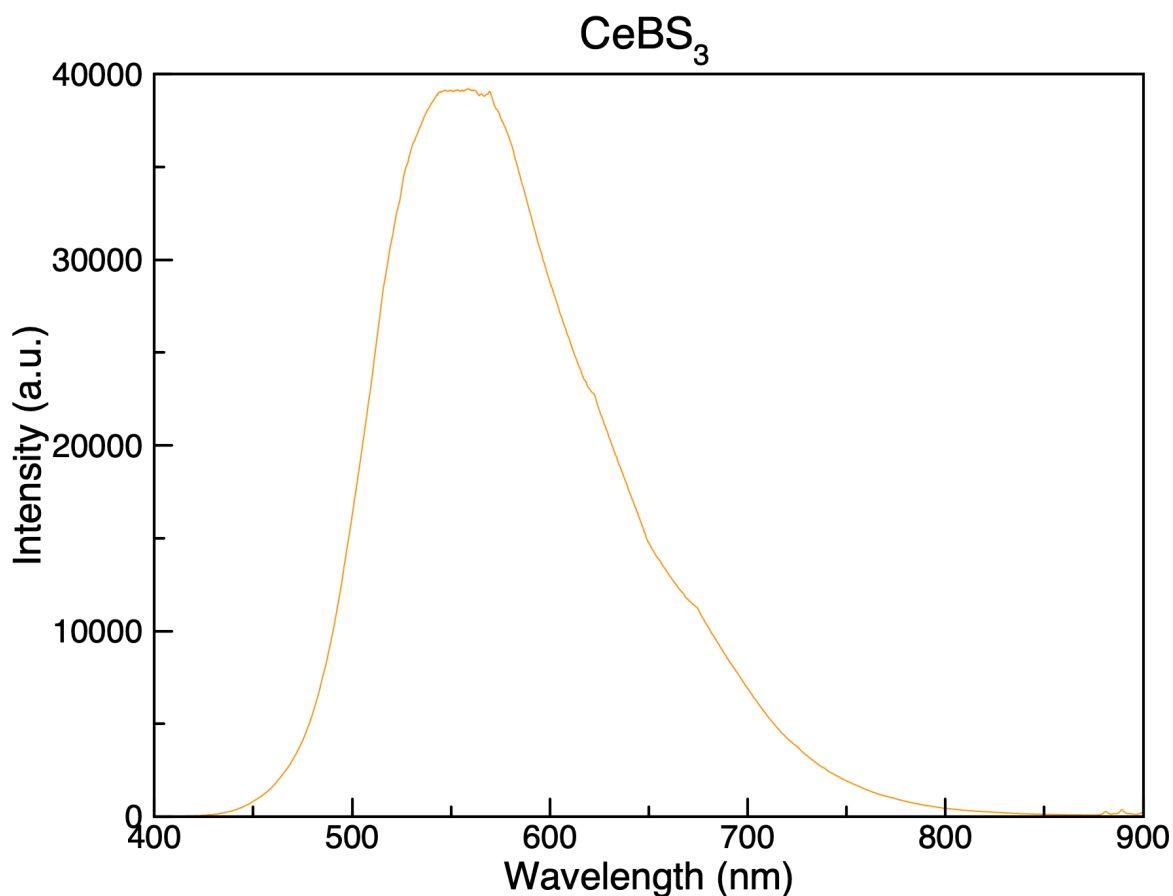


Figure S7. Fluorescence data obtained on a single crystal of CeBS₃ using an excitation wavelength of 375 nm. A single broad peak which covered much of the visible range measured was observed for CeBS₃, a phenomenon observed in other cerium compounds.⁸⁻¹¹

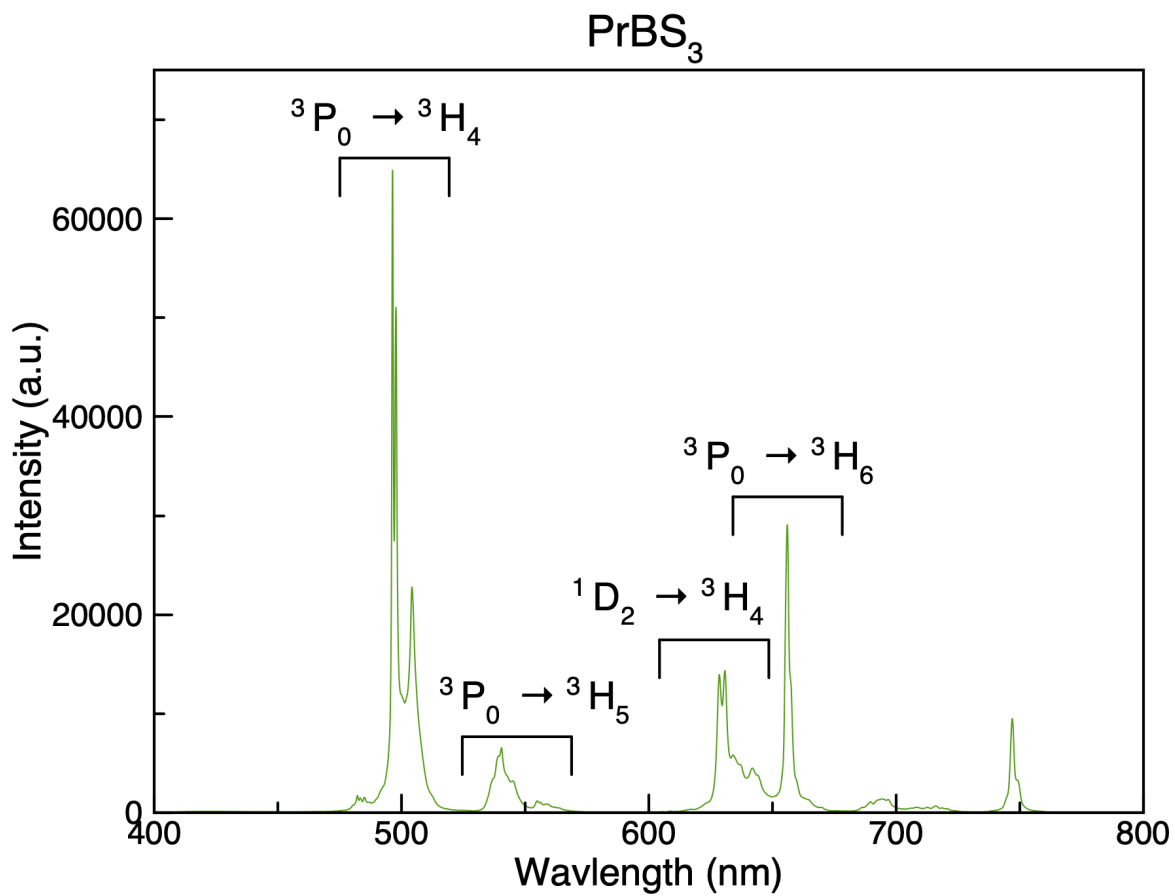


Figure S8. Fluorescence data obtained on a single crystal of PrBS_3 . The expected ${}^3\text{P}_0 \rightarrow {}^3\text{H}_4$, ${}^3\text{P}_0 \rightarrow {}^3\text{H}_5$, ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$, ${}^3\text{P}_0 \rightarrow {}^3\text{H}_6$ f-f transitions were observed.^{9, 12}

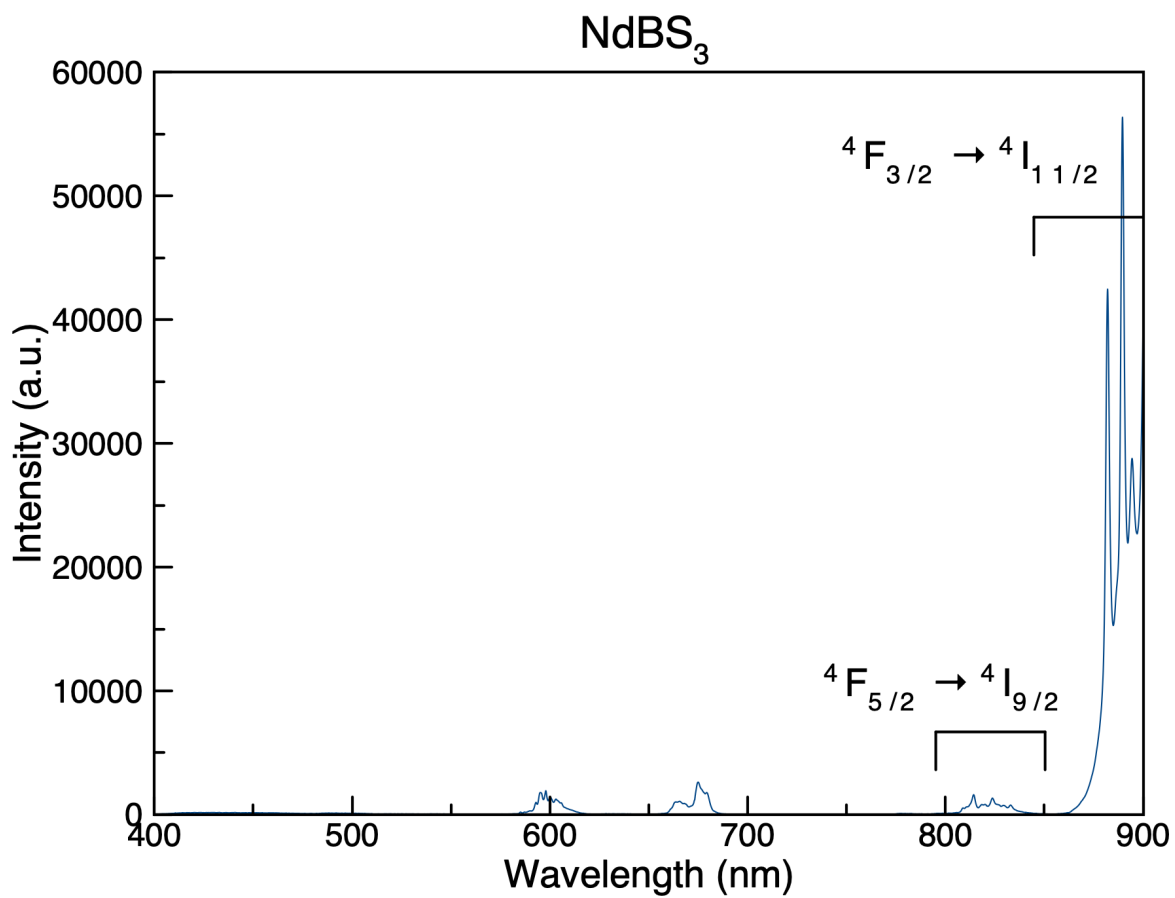


Figure S9. Fluorescence data obtained on a single crystal of NdBS₃. The characteristic ${}^4F_{5/2} \rightarrow {}^4I_{9/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ f-f transitions were resolved.¹³

8. BaB₂S₄ Synthesis Details

BaB₂S₄ was synthesized by combining 0.59 mmol BaS (99.7%, Alfa Aesar), 3.07 mmols B, 4.60 mmols S, 0.45 mmols K₂S, and 0.25 grams of a NaI-CsI eutectic flux into a carbon crucible (0.5 in OD x 0.25 in ID x 2 in L) fitted with a carbon cap. The crucible was placed inside a carbon-coated fused silica tube which was evacuated, sealed, and placed in a furnace set to step to 400 °C and then ramp to 550 °C in 2 hours where it dwelled for 48 hours. The furnace then slow-cooled to 350 °C in 20 hours and was then shut off to return to room temperature. To isolate the single crystals, the flux was dissolved in methanol, aided by sonication, and the crystals isolated via vacuum filtration.

9. Phase Pure BaB₂S₄ PXRD

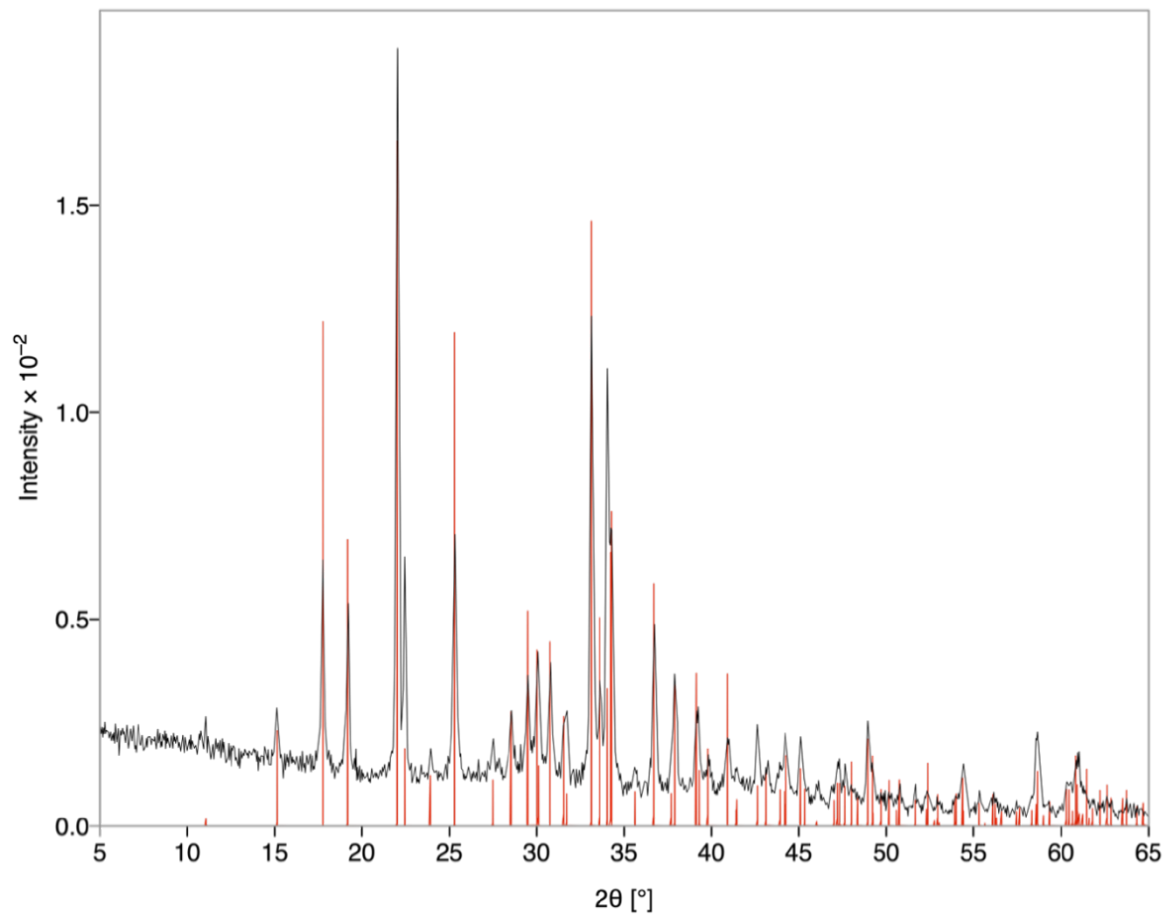


Figure S10. Powder X-ray Diffraction Pattern of phase pure BaB₂S₄ synthesized using our low temperature route.

10. Image of obtained single crystals of BaB₂S₄

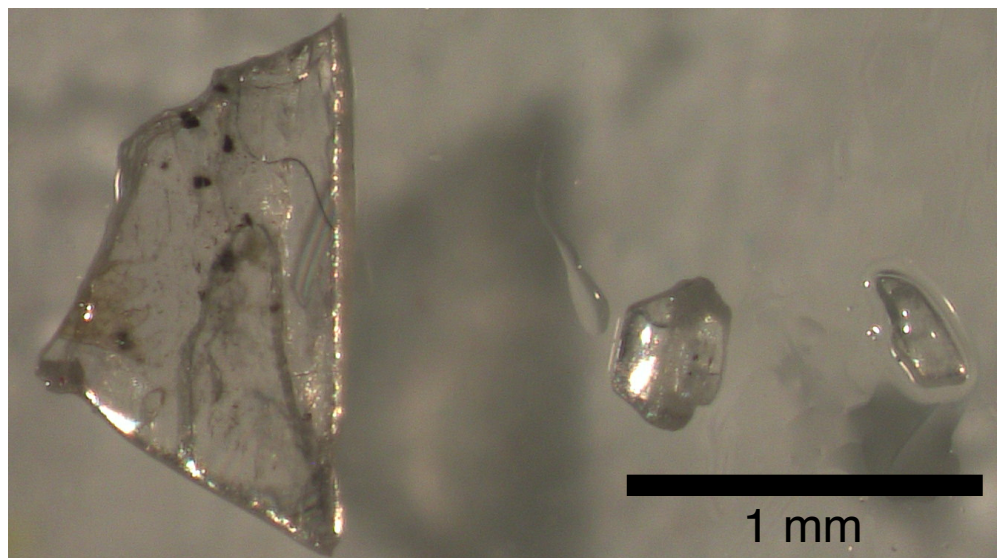


Figure S11. Image of the BaB₂S₄ crystals obtained using our low temperature synthetic route.

11. LaBS₃ Tauc Plot

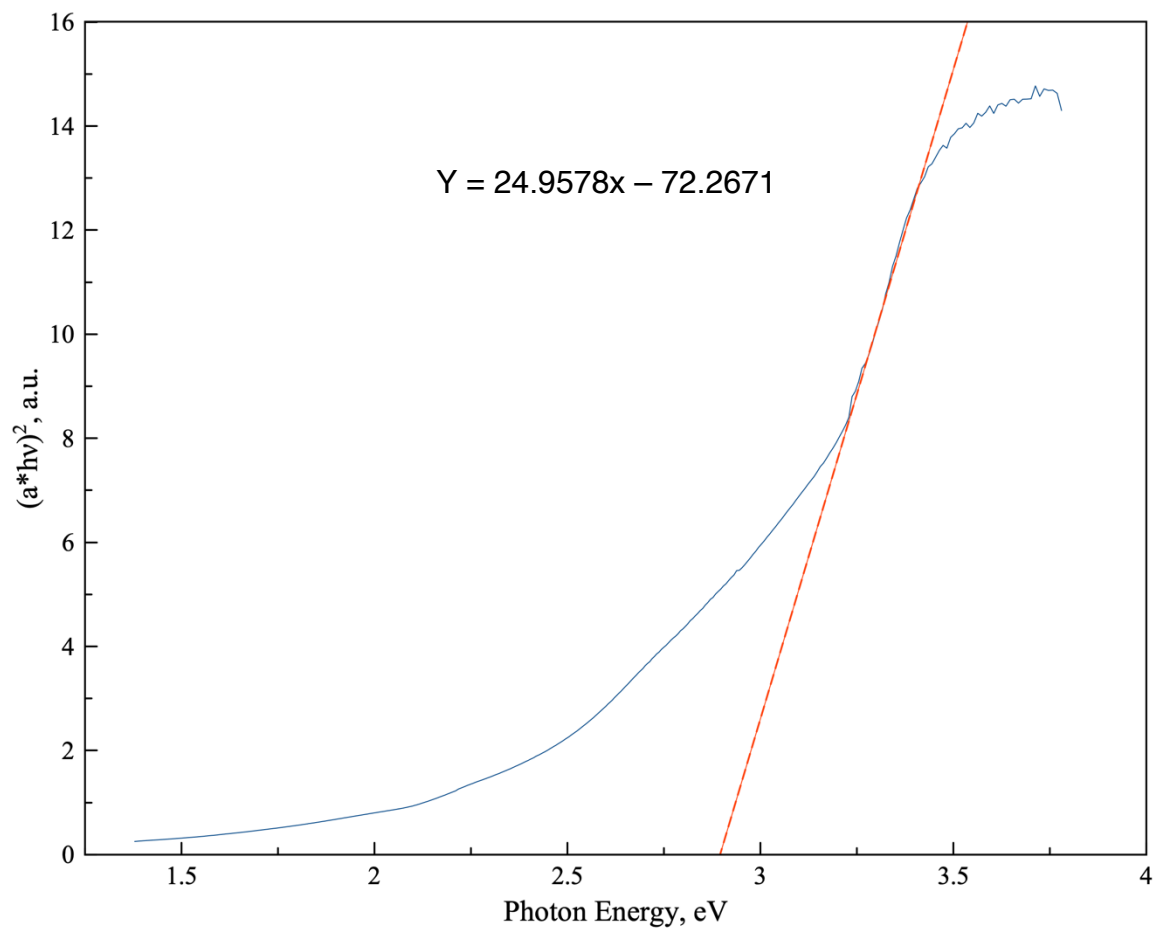


Figure S12. The Tauc plot created from the absorbance data for LaBS₃. A band gap of 2.9 eV was calculated which corresponds well to the yellow color of the LaBS₃ crystals.

12. SI REFERENCES

- (1) Liao, J. H., Varotsis, C., and Kanatzidis, M. G., *Inorg. Chem.*, 1993, **32**, 2453-2462
- (2) APEX3 Version 2019.1-0 and SAINT+ Version 8.40A., 2019, Bruker Nano, Inc., Madison, WI, United States.
- (3) Krause, L., Herbst-Irmer, R., Sheldrick, G. M., and Stalke, D., *J. Appl. Crystallogr.*, 2015, **48**, 3-10
- (4) Sheldrick, G. M., *Acta Crystallogr. A*, 2015, **71**, 3-8
- (5) Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., and Puschmann, H., *J. Appl. Crystallogr.*, 2009, **42**, 339-341
- (6) Sheldrick, G. M., *Acta Crystallogr. A*, 2008, **64**, 112-122
- (7) Kubelka, P., and Munk, F., *Z. Technol Phys*, 1931, **12**, 593
- (8) Banks, E., and Ward, R., *J. Electrochem. Soc.*, 1949, **96**, 297-303
- (9) Breton, L. S., Smith, M. D., and zur Loye, H.-C., *CrystEngComm*, 2021, **23**, 5241-5248
- (10) Hazin, P. N., Lakshminarayan, C., Brinen, L. S., Knee, J. L., Bruno, J. W., Streib, W. E., and Folting, K., *Inorg. Chem.*, 1988, **27**, 1393-1400
- (11) Klepov, V. V., Kocevski, V., Besmann, T. M., and zur Loye, H.-C., *CrystEngComm*, 2021, **23**, 831-840
- (12) Lin, Y.-F., Chang, Y. H., Chang, Y.-S., Tsai, B.-S., and Li, Y.-C., *J. Electrochem. Soc.*, 2006, **153**, G543-G547
- (13) Gui, Y., Yang, Q., Shao, Y., and Yuan, Y., *J. Lumin.*, 2017, **184**, 232-234