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Supporting Information

LaBS₃ Revisited: A Promising Mid-Infrared Nonlinear Optical material

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Section S1 Synthesis and Methods

1. Synthesis.

Li₂S (99.9%) and La₂S₃ (99.9%) were purchased from Beijing Hawk Science & Technology Co., Ltd while amorphous B (99.9%) and S (99.9%) powders were purchased from Shanghai Aladdin biochemistry technology Co., Ltd.

The LBS crystals were synthesized by a solid-state reaction under vacuum. In a glove box filled with argon gas, the Li₂S, La₂S₃, amorphous B and S powders with molar ratio of 1:1:4:6 and a total weight of 0.3 grams were loaded into a graphite crucible inside a quartz tube. The quartz tubes were then evacuated to reach a high vacuum of 10⁻³ Pa and sealed with a hydrogen-oxygen flame. The quartz tube was placed into a computer-controlled muffle furnace, heated to 750°C after 25 h and held at 750 °C for 36 h, then cooled to 650 °C at 10 °C/min and dwelled for 36 h, and finally cooled to 300 °C at 10 °C/min and turning the furnace off. The millimeter sized pale orange opaque LBS crystals (Figure S1) were obtained after washing the product with deionized water and ethanol. The microcrystalline powder samples used for various measurements were obtained by grinding the LBS crystals.

2. Methods

Single Crystal X-ray Diffraction

Single-crystal X-ray diffraction data for LBS were collected at 293 K using an Agilent SuperNova dual-wavelength CCD diffractometer with Mo K_{α} radiation ($\lambda = 0.71073$ Å). The CrysAlis Pro software package was utilized for data reduction. Numerical absorption correction based on Gaussian integration over a multifaceted crystal model and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm were applied^{S1}. The structure was determined by direct method and refined using full-matrix least-squares fitting on F^2 with SHELXL-

2016/6^{S2}. PLATON^{S3} was used for checking symmetry elements and no higher was given. Crystal data were summarized in table S1.

Powder X-ray Diffraction

Powder x-ray diffraction data were collected via Rigaku MiniFlex600 diffractometer. Scanning was performed with a scan step width of 0.02° using Cu K α radiation ($\lambda = 1.541886$ Å) in the 2 θ range of $10 - 70^{\circ}$.

Energy-Dispersive X-ray Spectroscopy

Elemental analyses were carried out using a field-emission scanning electron microscope (JSM6700F) outfitted with an Oxford INCA energy-dispersive X-ray spectroscope.

Infrared Spectrum

A Nicolet Magna 750 Fourier Transform Infrared spectrometer was utilized to measure the infrared (IR) spectrum. LBS powder weighing one percent was mixed well with pure dry KBr and the measuring spectral region is 4000 to 400 cm⁻¹.

UV-Vis-NIR diffuse reflectance spectroscopy

The ultraviolet - visible - near-IR (UV-Vis-NIR) diffuse reflectance spectrum in the range of 200-2000nm was collected using a PerkinElmer Lambda 950 UV–vis–NIR spectrophotometer, with a barium sulfate powder plate as a 100% reflectance reference. Absorption data is converted from the reflection data by the Kubelka - Munk function $\alpha/S = (1 - R)^2/2R$ (α is the absorption coefficient, S the scattering coefficient, and R the reflectance. The band gap value is the abscissa of the intersection of the absorption edge extension line and the zero absorption.

Second-harmonic Generation

SHG response measurements were performed using the Kurtz and Perry method with a 2.05 μ m Q-

switched laser ^{S4}. Grind the crystals and sieve them into particle size ranging from 45-53, 53-75, 75-105, 105-150, 150-210 and 210-300 µm, using microcrystalline AgGaS₂ with the same particle size range as a reference. The sample was placed on a glass microscope-covered slide, secured with a 1 mm thick silicone insole and a 5 mm diameter hole, and then covered with another glass slide. They were then placed into small tight boxes and probed under the pulsed infrared beam of a Q-switched Ho: Tm: Cr: YAG laser. The SHG signal was recorded on an oscilloscope connected to the detector. Standard IR NLO material of AgGaS₂ was used for all steps.

LIDT measurement

LIDT was measured using a 1 Hz 1064 nm Q-switch laser with $AgGaS_2$ as a reference. 150-210 μ m particle size sample box was picked out for this test. For a point on the optical element (sample box), increasing pulse energy was raised from 1 mJ until the point is damaged.

Thermal Analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a NETZCH STA 449F3 unit under N_2 atmosphere, at a heating rate of 15K/min.

Computational Method

Theoretical calculations were performed using the single crystal structure data for LBS. The electronic structure and optical properties were analyzed by the plane wave pseudopotential method in the density functional theory (DFT) implemented in the total energy code CASTEP. ^{S5, S6} For the exchange and correlation functions, we chose Perdew-Burke-Ernzerhof (PBE) in the generalized Gradient Approximation (GGA) ^{S7}. The interactions between the ionic cores and the electrons were described by the norm-conserving pseudopotential ^{S8}. The following valence-electron configurations were considered in the computation: La 5d¹6s², B 2s²2p¹, S 3s²3p⁴. The numbers of plane waves

included in the basis sets were determined by cutoff energies of 650 eV. Monkhorst-Pack k-point sampling of $3 \times 4 \times 3$ was used to perform numerical integration of the Brillouin zone for LBS. During the optical property calculations, approximately 96 empty bands were involved to ensure the convergence of linear optical properties and SHG coefficients for LBS. The calculations of second-order NLO susceptibilities were based on length-gauge formalism within the independent particle approximation^{S8}. The second-order NLO susceptibility can be expressed as

$$\chi abc L(-2\omega; \omega, \omega) = \chi abc \text{ inter } (-2\omega; \omega, \omega) + \chi abc \text{ intra} (-2\omega; \omega, \omega) + \chi abc \text{ mod} (-2\omega; \omega, \omega)$$

where the subscript L denotes the length gauge, χabc inter, χabc intra and χabc mod give the contributions to χabc L from interband processes, intraband processes, and the modulation of interband terms by intraband terms, respectively.

Formula	LaBS ₃
formula weight	245.90
temperature (K)	293(2)
crystal system	orthorhombic
space group	<i>Pna</i> 2 ₁ (No. 33)
a (Å)	7.6759(10)
b (Å)	6.0392(6)
c (Å)	8.9841(10)
V (Å ³)	416.47(8)
Z	4
ρ_{calc} (g/cm ³)	3.922
μ (mm ⁻¹)	11.528
F(000)	440.0
λ (Mo Ka) (Å)	0.71073
R _{int}	0.0307
Goodness-of-fit on F ²	1.049
$R_1, wR_2 [I \ge 2\sigma (I)]^a$	0.0307, 0.0618
R_1 , wR_2 (all data)	0.0338, 0.0633
flack parameter	-0.06(5)

Table S1. Crystallographic data and structure refinement parameters for LaBS₃.

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; \text{ and } wR_{2} = \{\Sigma [w(F_{o}{}^{2} - F_{c}{}^{2})^{2}] / \Sigma [w(F_{o}{}^{2})^{2}] \}^{1/2}.$

Atom	x	y	Z	U(eq)
La(1)	3870(1)	4292(1)	6887(2)	8(1)
B(1)	1470(16)	4078(16)	3604(14)	10(2)
S(1)	33(3)	4091(3)	2015(5)	12(1)
S(2)	1747(4)	1666(5)	4801(3)	10(1)
S(3)	2965(4)	6374(5)	3937(3)	10(1)

Table S2. Fractional atomic coordinates (×10⁴) and equivalent Isotropic displacement parameters (Å²×10³) for LBS. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Table S3. Selected bond distances (Å), BV and BVS for LBS.

$LaBS_3$			
Bond	Length	BV	BVS
La(1)-S(3)#1	2.912(3)	0.483	
La(1)-S(2)	2.947(3)	0.440	
La(1)-S(2)#2	2.954(3)	0.431	
La(1)-S(3)	3.015(3)	0.366	
La(1)-S(1)#3	3.0200(17)	0.361	3.195
La(1)-S(2)#3	3.022(3)	0.359	
La(1)-S(3)#4	3.075(3)	0.311	
La(1)-S(1)#5	3.153(2)	0.252	
La(1)-S(1)#1	3.2542(18)	0.192	
B(1)-S(1)	1.804(14)	1.030	
B(1)-S(2)	1.823(11)	0.979	2.985
B(1)-S(3)	1.824(12)	0.976	

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2, y-1/2, z+1/2; #2 x+1/2, -y+1/2, z; #3 -x+1/2, y+1/2, z+1/2; #4 -x+1, -y+1, z+1/2; #5 -x, - y+1, z+1/2

Table S4. Measured LDTs of LBS and AGS.

Compounds	Damage Energy (mJ)	Spot area (cm ²)	Damage threshold (MW/cm ²)
LBS	12.61	0.025	49.55
AGS	0.89	0.025	3.50

independent SHG tensors	Values (pm/V)
$d_{15} = d_{31}$	3.19
$d_{24} = d_{32}$	11.00
<i>d</i> ₃₃	11.20

Table S5. The values of independent SHG tensor for LBS.



Figure S1. Photograph of LBS crystals.



Figure S2. Simulated and measured powder X-ray diffraction patterns for LBS.



Figure S3. EDS spectrum of LBS.



Figure S4. TGA and DSC curves for LBS under a N_2 atmosphere.



Figure S5. IR spectrum for LBS.



Figure S6. UV-vis-IR spectrum for LBS



Figure S7. Calculated band structure of LBS.



Figure S8. The density of states for LBS.



Figure S9. The calculated refractive indices for LBS

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