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Supporting Information

$Ba_3(BS_3)(PS_4)$: The First Alkaline-Earth Metal Thioborate-Thiophosphate with Strong Optical Anisotropy Originated from Planar $[BS_3]$ Units

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Experimental Procedures

Reagents and Synthesis. All the raw reagents (BaS, B, P, S) with high purity (≥ 99.99 %) were commercially purchased by Aladdin Industrial Inc., and were stored in a dry Ar-filled glove box with limited oxygen and moisture levels below 0.1 ppm. The $Ba_3(BS_3)(PS_4)$ single crystal for structural determination was prepared by the high temperature solution method. The starting materials BaS, B, P and S were weighed and loaded into graphite crucibles with the ratio of 3 : 1 : 1 : 4. The silica tubes were sealed with methane-oxygen flame under a high vacuum of 10^{-3} Pa. After that, the sealed tubes were put into a computer-controlled furnaces and heating program setting to 900 °C in 20 h, kept at the temperature for 24 h, then the temperature was cooled to room temperature at a rate of 1 °C/h. Finally, the colorless single crystals for the title compound were obtained.

Single-Crystal X-ray Diffraction (XRD). High-quality transparent single crystal was selected under an optical microscope for collecting the X-ray diffraction data. A Bruker SMART APEX II CCD single crystal X-ray diffractometer using graphite-monochromatized molybdenum Kα radiation (λ = 0.71073 Å) was performed to collect the crystal data at room temperature. After collection, the SADABS program[1] was used to perform the multiscan-type absorption correction of the structure data. After that, the XPREP program in the SHELXTL program package was used to determine the space group, and the SHELXT and XL programs were applied to solve and refine the structure data by direct methods.[2] Finally, the PLATON program was used to check the possible missing symmetry elements, and no higher symmetry was found.[3]

Powder X-ray diffraction (PXRD). The Bruker D2 PHASER diffractometer with Cu Kα radiation (λ = 1.5418 Å) was applied to determine the purity of powder samples. The experimental PXRD patterns were recorded from 10° to 70° (2θ) with a scan rate of 0.02°. After then, the powder rietveld refinement has been implemented by using GSAS software.

Energy-Dispersive X-ray Spectroscopy (EDS). The EDS spectrum and mapping of $Ba_3(BS_3)(PS_4)$ crystal were characterized on a field emission scanning electron microscope (FE-SEM, JEOL JSM-7610F Plus, Japan) equipped with an energy-dispersive X-ray spectrometer (Oxford, X-Max 50). It was operated at 5 kV, and the EDS spectrum and mappings confirm the existence of Ba, B, P and S elements in the crystal.

Raman Spectroscopy. Hand-picked $Ba_3(BS_3)(PS_4)$ crystals were first placed on object slides and then Raman spectra were recorded by a 532 nm laser in the 4000-100 cm^{-1} region using a LABRAM HR Evolution spectrometer equipped with a CCD detector, The integration time was set to 5 seconds.

UV-vis-NIR Diffuse Reflectance Spectroscopy and IR Spectroscopic Measurements. The UV-vis-NIR diffuse-reflectance spectrum of pure phase $Ba_3(BS_3)(PS_4)$ powder samples was collected on a SolidSpec-3700 DUV spectrophotometer at room temperature. The measured wavelength range is 200-2600 nm. To figure out the experimental band gap, the collected data were converted to absorbance by the Kubelka-Munk function[4] $F(R) = \alpha/S = (1 - R)^2/2R$, where F(R): the ratio of absorption coefficient to scattering coefficient; α: absorption coefficient; R: reflectance; S: scattering coefficient. The IR spectrum was recorded on a Shimadzu IRAffinity-1 Fourier transform infrared spectrometer with a resolution of 2 cm^{-1}, covering the wavenumber range from 400 to 4000 cm^{-1}.

Thermal analysis. Differential scanning calorimetry (DSC) was performed with a simultaneous NETZSCH STA 449C thermal analysis instrument. Approximately 10 mg of the polycrystalline powders were ground and then placed in a small silica tube that was subsequently sealed. The tube was heated from room temperature to 1000 °C, and then cooled to room temperature with the heating/cooling rate both at 15 °C min^{-1}.

Theoretical Calculations. The band structure, total/partial density of states, and optical properties of $Ba_3(BS_3)(PS_4)$ were calculated by using the plane-wave pseudopotential method implemented in the CASTEP[5] based on the density functional theory (DFT) method. Perdew-Burke-Ernzerhof (PBE)[6] exchange-correlation of Generalized Gradient Approximation (GGA)[7] was applied in the calculation. The interactions between core and electron were described by the norm-conserving pseudopotential (NCP).[8] The Monkhorst−Pack schemes was set as 4 × 5 × 2 for $Ba_3(BS_3)(PS_4)$. The valence electrons were set as Ba $5p^5$ $6s^2$ B $2s^22p^1$, P $3s^23p^3$ and S $3s^2$ $3p^4$ for $Ba_3(BS_3)(PS_4)$. The kinetic energy cutoffs were set to be 650 eV. The HOMO-LUMO gap, polarizability anisotropy and hyperpolarizability of the $[BQ_3]$ and $[PQ_4]$ (Q = O, S) groups were investigated by Gaussian 09 package under the condition of the B3LYP at 6-31G.

Refractive Index Difference (RID) Measurement. The RIDs of $Ba_3(BS_3)(PS_4)$ were estimated by the polarizing microscope equipped (ZEISS Axio Scope. 5 pol) with Berek compensator. Different single crystals with different orientations were used for the measurements. The wavelength of the light source is 546 nm. The RID values are calculated by the formula: RID = δ/d, where δ is the optical path difference, and d represents the thickness of the single crystal**.**

Table S1. Crystal data and structure refinements of $Ba_3(BS_3)(PS_4)$.

Empirical formula	$Ba_3(BS_3)(PS_4)$
Formula weight (Da)	678.22
Temperature (K)	298
Crystal system, space group	orthorhombic, *Pnma*
Unit cell dimensions (Å)	a = 8.8167(3) b = 6.5913(2) c = 21.1218(7)
Volume (Å^3)	1227.46(7)
Z	4
Calculated density (Mg/m^3)	3.670
Completeness (%)	96.87
Absorption coefficient (mm^{-1})	10.783
F(000)	1200
2θ range for data collection/°	5.006 to 51.434
Index ranges	$-10 \leqslant h \leqslant 10, -8 \leqslant k \leqslant 8, -25 \leqslant l \leqslant 25$
Reflections collected	15001
Independent reflections	1236 [R_{int} = 0.0447, R_{sigma} = 0.0204]
Observed reflections [I>2σ(I)]	1224
Data/restraints/parameters	1236/0/67
Absorpt correction type	multi-scan
Goodness-of-fit on F^2	1.202
Final R indices ($F_o^2 > 2\sigma(F_o^2)$)^a	R_1 = 0.0138, wR_2 = 0.0308
R indices (all data)^a	R_1 = 0.0141, wR_2 = 0.0310
Largest diff. peak and hole (e·Å^{-3})	0.45 and -0.65

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/ \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Atomic coordinates, equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS of $Ba_3(BS_3)(PS_4)$.

Atoms	x	y	z	U_{eq}	Wyckoff positions	BVS[a]
Ba1	0.48833(2)	0.25	0.57638(2)	14.60(7)	4*c*	2.285
Ba2	0.100465(2)	0.25	0.60117(2)	17.41(7)	4*c*	1.995
Ba3	0.58570(2)	0.75	0.72527(2)	18.53(7)	4*c*	2.178
B1	0.7607(4)	0.25	0.77389(17)	14.4(7)	4*c*	3.030
P1	0.75951(10)	0.75	0.55704(4)	14.51(17)	4*c*	5.429
S1	0.78583(8)	0.49898(8)	0.50259(3)	18.12(14)	8*d*	2.205
S2	0.90501(11)	0.75	0.63143(4)	21.63(19)	4*c*	2.007
S3	0.53506(10)	0.75	0.58134(4)	17.46(18)	4*c*	2.416
S4	0.70724(11)	0.25	0.69053(4)	24.0(2)	4*c*	1.949
S5	0.77799(7)	0.48415(9)	0.81832(3)	17.96(13)	8*d*	2.068

[a] The bond valence sum is calculated by bond-valence theory ($S_{ij} = \exp[(R_0-R)/B$, where R is an empirical constant, R_0 is the length of bond I (in angstroms), and B= 0.37).

Table S3. Selected bond lengths of Ba$_3$(BS$_3$)(PS$_4$).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ba1	S1	3.4645(7)	Ba2	S2	3.4701(3)
Ba1	S1^{2}	3.3709(6)	Ba2	S2^{7}	3.4701(3)
Ba1	S1^{3}	3.3709(6)	Ba2	S4	3.2308(10)
Ba1	S1^{4}	3.4644(7)	Ba2	B1^{10}	3.473(4)
Ba1	S5^{5}	3.2814(6)	Ba3	S5^{12}	3.3584(6)
Ba1	S5^{6}	3.2814(6)	Ba3	S5^{5}	3.3584(7)
Ba1	S3^{7}	3.32294(15)	Ba3	S5	3.1317(6)
Ba1	S3^{3}	3.3377(8)	Ba3	S5^{13}	3.1317(6)
Ba1	S3	3.32295(16)	Ba3	S3	3.0726(9)
Ba1	P1^{3}	3.5659(9)	Ba3	S2	3.4429(10)
Ba1	S4	3.0884(9)	Ba3	S2^{5}	3.4203(9)
Ba2	S1^{8}	3.3096(6)	Ba3	S4^{14}	3.5423(4)
Ba2	S1^{9}	3.3096(6)	Ba3	S4	3.5423(4)
Ba2	S1^{4}	3.2789(6)	B1	S4	1.823(4)
Ba2	S1	3.2790(6)	B1	S5	1.813(2)
Ba2	S5^{10}	3.3288(6)	P1	S1	2.0283(7)
Ba2	S5^{11}	3.3288(6)	P1	S2	2.0286(12)

^{1}-1+X,+Y,+Z; ^{2}1-X,-1/2+Y,1-Z; ^{3}1-X,1-Y,1-Z; ^{4}+X,1/2-Y,+Z; ^{5}-1/2+X,+Y,3/2-Z; ^{6}-1/2+X,1/2-Y,3/2-Z; ^{7}+X,-1+Y,+Z; ^{8}2-X,-1/2+Y,1-Z; ^{9}2-X,1-Y,1-Z; ^{10}1/2+X,+Y,3/2-Z; ^{11}1/2+X,1/2-Y,3/2-Z; ^{12}-1/2+X,3/2-Y,3/2-Z; ^{13}+X,3/2-Y,+Z; ^{14}+X,1+Y,+Z

Table S4. Selected angles (°) of Ba$_3$(BS$_3$)(PS$_4$).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S1^{4}	Ba1	S1^{2}	123.560(11)	S1^{9}	Ba2	S2^{7}	137.568(19)
S1^{3}	Ba1	S1^{4}	58.79(2)	S1^{2}	Ba2	S2^{7}	59.515(17)
S1^{2}	Ba1	S1	56.549(19)	S1	Ba2	S2	59.515(17)
S1^{3}	Ba1	S1	123.559(11)	S1	Ba2	S2^{7}	116.318(18)
S1^{4}	Ba1	S1	95.036(16)	S5^{11}	Ba2	S5^{12}	55.24(2)
S1^{3}	Ba1	S1^{2}	95.037(16)	S5^{11}	Ba2	S2	69.444(18)
S5^{6}	Ba1	S1	120.666(14)	S5^{12}	Ba2	S2^{7}	69.443(18)
S5^{5}	Ba1	S1^{2}	120.665(14)	S5^{12}	Ba2	S2	121.972(18)
S5^{5}	Ba1	S1^{4}	99.263(16)	S5^{11}	Ba2	S2^{7}	121.972(18)
S5^{6}	Ba1	S1^{4}	72.498(15)	S2	Ba2	S2^{7}	143.51(3)
S5^{6}	Ba1	S1^{2}	162.863(16)	S4	Ba2	S1^{10}	147.125(13)
S5^{5}	Ba1	S1	162.864(16)	S4	Ba2	S1^{9}	147.125(12)
S5^{6}	Ba1	S1^{3}	99.263(16)	S4	Ba2	S1	83.883(18)
S5^{5}	Ba1	S1^{3}	72.498(15)	S4	Ba2	S1^{2}	83.882(18)
S5^{6}	Ba1	S5^{5}	56.11(2)	S4	Ba2	S5^{11}	106.810(18)
S5^{5}	Ba1	S3^{7}	65.307(18)	S4	Ba2	S5^{12}	106.810(18)
S5^{5}	Ba1	S3^{4}	129.910(17)	S4	Ba2	S2^{7}	71.756(16)
S5^{6}	Ba1	S3^{7}	121.008(19)	S4	Ba2	S2	71.756(16)
S5^{6}	Ba1	S3^{4}	129.910(17)	S5	Ba3	S5^{13}	68.05(2)
S5^{6}	Ba1	S3	65.306(18)	S5^{6}	Ba3	S5^{14}	62.90(2)
S5^{5}	Ba1	S3	121.007(18)	S5^{13}	Ba3	S5^{14}	108.506(17)
S3^{7}	Ba1	S1^{4}	126.250(18)	S5	Ba3	S5^{6}	108.506(18)
S3	Ba1	S1^{2}	112.963(19)	S5	Ba3	S5^{14}	154.331(15)
S3^{7}	Ba1	S1^{2}	56.669(17)	S5^{13}	Ba3	S5^{6}	154.331(15)
S3	Ba1	S1	56.669(18)	S5^{6}	Ba3	S2^{6}	82.318(18)
S3^{4}	Ba1	S1^{3}	57.440(16)	S5	Ba3	S2^{6}	72.349(18)
S3	Ba1	S1^{3}	126.251(18)	S5^{13}	Ba3	S2	85.332(17)
S3	Ba1	S1^{4}	67.523(18)	S5^{6}	Ba3	S2	120.183(16)
S3^{4}	Ba1	S1	66.280(17)	S5^{14}	Ba3	S2^{6}	82.318(18)
S3^{7}	Ba1	S1^{3}	67.522(18)	S5^{14}	Ba3	S2	120.183(16)
S3^{4}	Ba1	S1^{2}	66.281(17)	S5	Ba3	S2	85.332(17)
S3^{4}	Ba1	S1^{4}	57.440(16)	S5^{13}	Ba3	S2^{6}	72.349(18)
S3^{7}	Ba1	S1	112.962(19)	S5	Ba3	S4	56.336(18)
S3^{7}	Ba1	S3	165.30(3)	S5^{13}	Ba3	S4^{15}	56.336(18)
S3	Ba1	S3^{4}	92.243(15)	S5^{14}	Ba3	S4^{15}	72.670(18)
S3^{7}	Ba1	S3^{4}	92.242(15)	S5^{13}	Ba3	S4	119.132(19)
S4	Ba1	S1	82.997(19)	S5^{6}	Ba3	S4^{15}	132.301(19)
S4	Ba1	S1^{4}	146.557(13)	S5^{6}	Ba3	S4	72.671(19)
S4	Ba1	S1^{2}	82.996(19)	S5^{14}	Ba3	S4	132.302(19)
S4	Ba1	S1^{3}	146.557(13)	S5	Ba3	S4^{15}	119.132(19)
S4	Ba1	S5^{5}	79.87(2)	S3	Ba3	S5	134.395(16)
S4	Ba1	S5^{6}	79.87(2)	S3	Ba3	S5^{6}	67.131(17)
S4	Ba1	S3	84.140(15)	S3	Ba3	S5^{14}	67.131(17)
S4	Ba1	S3^{4}	144.86(2)	S3	Ba3	S5^{13}	134.395(16)
S4	Ba1	S3^{7}	84.141(15)	S3	Ba3	S2	63.21(2)
S1^{2}	Ba2	S1^{10}	69.98(2)	S3	Ba3	S2^{6}	143.88(2)
S1^{2}	Ba2	S1^{9}	99.095(13)	S3	Ba3	S4^{15}	80.736(15)
S1^{2}	Ba2	S1	60.07(2)	S3	Ba3	S4	80.736(15)
S1^{10}	Ba2	S1^{9}	59.99(2)	S2^{6}	Ba3	S2	152.90(2)

S1	Ba2	S1^{10}	99.094(13)	S2^{6}	Ba3	S4^{15}	108.917(14)
S1	Ba2	S1^{9}	69.98(2)	S2	Ba3	S4^{15}	68.494(15)
S1^{2}	Ba2	S5^{11}	169.239(17)	S2^{6}	Ba3	S4	108.917(14)
S1	Ba2	S5^{12}	169.237(17)	S2	Ba3	S4	68.494(15)
S1^{9}	Ba2	S5^{12}	99.554(16)	S4^{15}	Ba3	S4	136.98(3)
S1^{10}	Ba2	S5^{11}	99.554(16)	S5^{2}	B1	S5	116.7(2)
S1^{10}	Ba2	S5^{12}	72.687(15)	S5	B1	S4	121.45(10)
S1^{9}	Ba2	S5^{11}	72.687(15)	S5^{2}	B1	S4	121.45(10)
S1^{2}	Ba2	S5^{12}	121.220(14)	S1^{13}	P1	S1	109.32(5)
S1	Ba2	S5^{11}	121.220(15)	S1^{13}	P1	S3	104.66(4)
S1^{10}	Ba2	S2	137.568(19)	S1	P1	S3	104.66(4)
S1^{10}	Ba2	S2^{7}	77.788(18)	S1	P1	S2	111.52(4)
S1^{2}	Ba2	S2	116.318(18)	S1^{13}	P1	S2	111.52(4)
S1^{9}	Ba2	S2	77.788(18)	S2	P1	S3	114.68(5)

^{1}-1+X,+Y,+Z; ^{2}+X,1/2-Y,+Z; ^{3}1-X,-1/2+Y,1-Z; ^{4}1-X,1-Y,1-Z; ^{5}-1/2+X,1/2-Y,3/2-Z; ^{6}-1/2+X,+Y,3/2-Z; ^{7}+X,-1+Y,+Z; ^{8}1+X,+Y,+Z; ^{9}2-X,1-Y,1-Z; ^{10}2-X,-1/2+Y,1-Z; ^{11}1/2+X,+Y,3/2-Z; ^{12}1/2+X,1/2-Y,3/2-Z; ^{13}+X,3/2-Y,+Z; ^{14}-1/2+X,3/2-Y,3/2-Z; ^{15}+X,1+Y,+Z

Table S5. Anisotropic displacement parameters ($Å^2×10^3$) for $Ba_3(BS_3)(PS_4)$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Ba1	15.02(12)	16.13(11)	12.66(11)	0	-1.61(7)	0
Ba2	15.41(12)	20.16(12)	16.66(12)	0	-1.63(7)	0
Ba3	19.16(12)	21.49(12)	14.95(11)	0	-3.95(8)	0
B1	11.8(18)	16.1(18)	15.4(16)	0	-1.0(14)	0
P1	15.5(4)	13.7(4)	14.3(4)	0	-2.0(3)	0
S1	21.0(3)	13.4(3)	19.9(3)	-2.1(2)	-2.6(2)	1.2(2)
S2	22.4(5)	24.1(5)	18.4(4)	0	-9.7(4)	0
S3	15.5(4)	19.9(4)	17.0(4)	0	0.0(3)	0
S4	25.8(5)	33.9(5)	12.4(4)	0	-4.1(3)	0
S5	23.6(3)	12.2(3)	18.1(3)	-0.1(2)	-3.9(2)	-0.3(2)

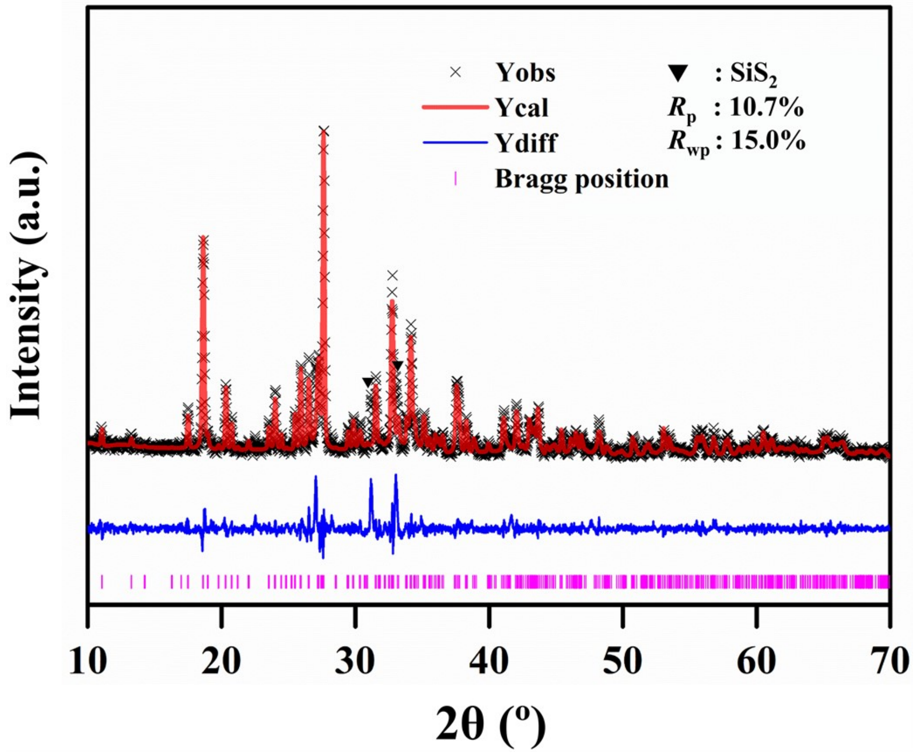

Figure S1. The Rietveld refinement PXRD of $Ba_3(BS_3)(PS_4)$.

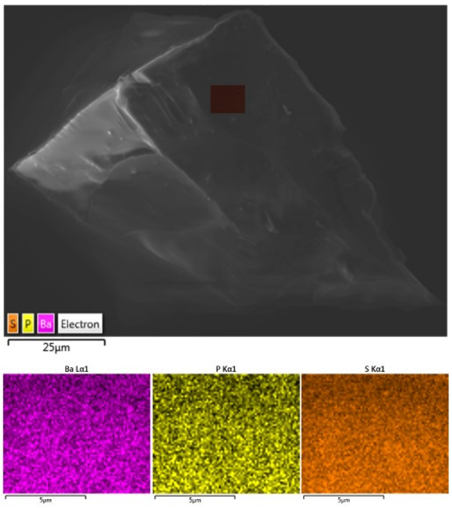

Figure S2. The SEM image and EDS mapping of $Ba_3(BS_3)(PS_4)$.

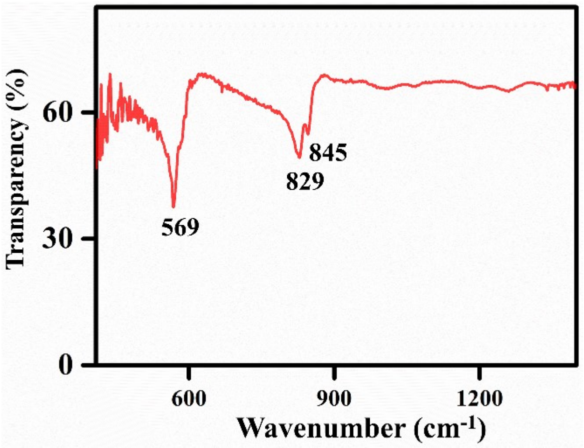

Figure S3. The IR absorption spectrum of $Ba_3(BS_3)(PS_4)$.

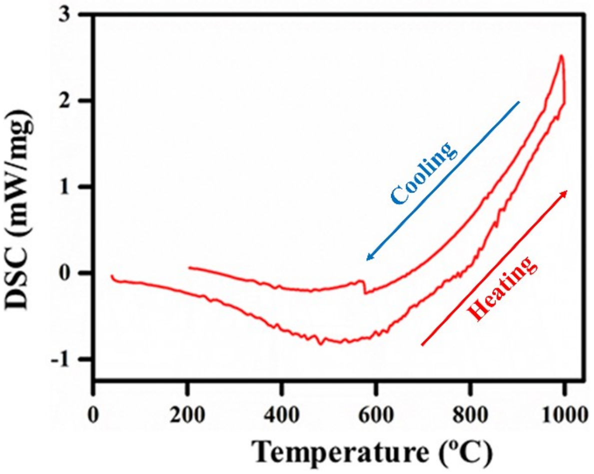

Figure S4. DSC curve of $Ba_3(BS_3)(PS_4)$.

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