

BaGeO₃: A Mid-IR Transparent Crystal with Super Strong Raman Response

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Experimental and Computational Methods

Growth of BaGeO₃ crystals. BaGeO₃ polycrystalline powder was synthesized by a traditional solid state reaction. Equimolar GeO₂ (99.9%, Aladdin) and BaCO₃ (99.0%, Sinopharm Chemical Reagent Co. Ltd.) were mixed in an agate mortar and then heated at 1000°C in a corundum crucible for 48 hours with an intermediate grind. The BaGeO₃ polycrystalline product was dissolved completely with a flux (an alkali borate or an alkali molybdate) in a platinum crucible. The solution temperature was carefully adjusted until the saturation point was reached. After that, a BaGeO₃ seed crystal was immersed in the saturated solution and grew by continuous cooling. The cooling rate was kept at 0.1°C/h during the growth process, and the crystal rotation rate was kept at 10 rpm. Finally, a transparent BaGeO₃ crystal was obtained. A typical XRPD pattern of the BaGeO₃ crystal is shown in Figure S1.

Single crystal structure determination. A single crystal of BaGeO₃ was used for structure determination. Data were collected on a Bruker SMART APEX II CCD diffractometer using graphite-monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296(2) K and integrated with the SAINT program. The calculations were performed using the crystal structure refinement program SHELXTL.¹ Refinement details are shown in Table S1. Atomic positions are listed in Tables S2; selected bond lengths and angles are presented in Figure S2.

Raman spectroscopy and IR spectroscopy. Raman spectra were recorded on a Horiba Jobin Yvon LabRAM HR Evolution Raman spectrometer. Raman scattering light was collected in a backscattering geometry using an optical confocal system equipped with a CCD detector. No polarization selection was applied in our experiments. The 355 nm line of a Q-switched THG-Nd:YAG pulsed laser was employed as the excitation source. The laser power was about 1.5 mW on the crystal samples. Every Raman spectrum was an average of 10 scans and each scanning time was 10 s. The spectral resolution was about 1.3 cm^{-1} . Prior to Raman measurements, the spectrometer was calibrated by reference to the 520 cm^{-1} standard line of a Si wafer. The IR spectrum of the BaGeO₃ crystal was collected using a Thermo Nicolet 8700 Fourier transform infrared spectrophotometer in the wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$.

Computational methods. Calculations for BaGeO₃ crystal Raman/IR spectra were performed using a plane-wave basis set and norm-conserving pseudopotentials within density functional theory (DFT) implemented in the Cambridge Sequential Total Energy Package (CASTEP).² The exchange and correlation effects were treated by the Wu–Cohen (WC) functional in the generalized gradient approximation (GGA).³ The valence electron configurations were $5s^25p^66s^2$ for barium, $3d^{10}4s^24p^2$ for germanium, and $2s^22p^4$ for oxygen. The convergence thresholds between two neighboring optimization cycles for the total energy change, maximum displacement, maximum force, and maximum stress were set as 10^{-6} eV/atom , 0.001 \AA , 0.03 eV/\AA , 0.05 GPa , respectively. The number of plane waves included in the basis set was determined by an energy cutoff of 1050 eV, and the numerical integration of the Brillouin zone was performed over a $2 \times 2 \times 1$ Monkhorst-Pack grid. All the computational parameters have been tested to ensure good convergence in the calculations.

References

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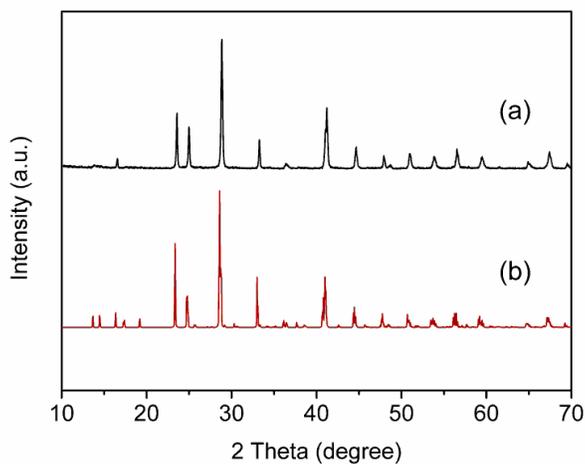


Figure S1. (a) Experimental and (b) calculated XRPD patterns of the BaGeO₃ single crystal.

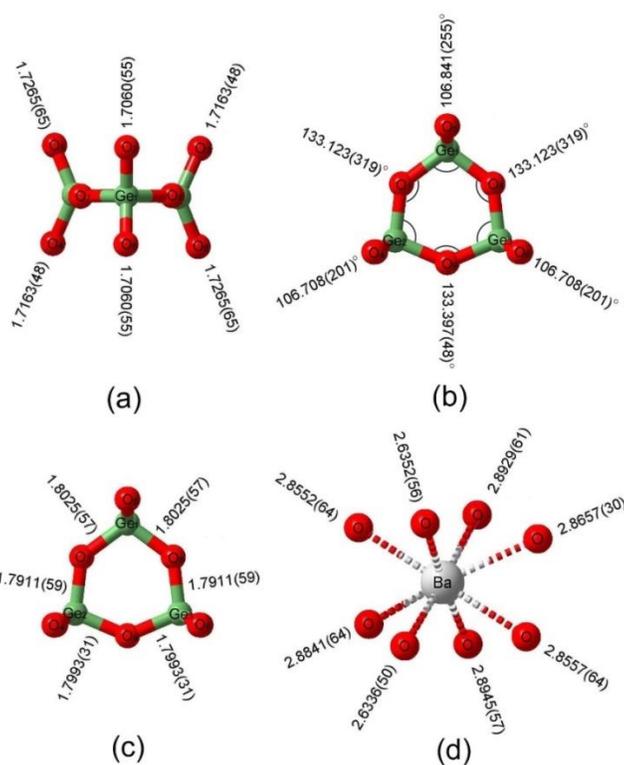
Table S1. Crystallographic Refinement Details for the BaGeO₃ Crystal

formula	BaGeO ₃
F_w (g·mol ⁻¹)	257.93
crystal system	Monoclinic
space group	C2/c
a (Å)	13.178(10)
b (Å)	7.626(6)
c (Å)	11.670(9)
α (°)	90
β (°)	111.638(8)
γ (°)	90
V (Å ³)	1090.0(14)
Z	12
ρ_c (g·cm ⁻³)	4.715
μ (mm ⁻¹)	18.855
λ (Mo $K\alpha$) (Å)	0.71073
T (K)	296
F (000)	1344.0
$R_1[F^2 > 2\sigma(F^2)]^a$	0.0267
$wR_2(F^2)^b$	0.0894

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}.$$

Table S2. Atomic Positions for the BaGeO₃ Crystal

atom	Wyckoff	x/a	y/b	z/c
Ba1	8f	0.41303(3)	0.25944(5)	0.50067(3)
Ba2	4c	1/4	1/4	0
O1	4e	1/2	0.1356(9)	3/4
O2	8f	0.3759(5)	0.0906(7)	0.8976(5)
O3	8f	0.2784(4)	0.0914(7)	0.6115(5)
O4	8f	0.3899(4)	0.1910(7)	0.2492(5)
O5	8f	0.4530(4)	0.4315(7)	0.1092(5)
Ge1	4e	1/2	0.33186(13)	1/4
Ge4	8f	0.37558(6)	0.04227(9)	0.75293(7)

**Figure S2.** Selected bond distances (Å) and bond angles (°) for the BaGeO₃ crystal.

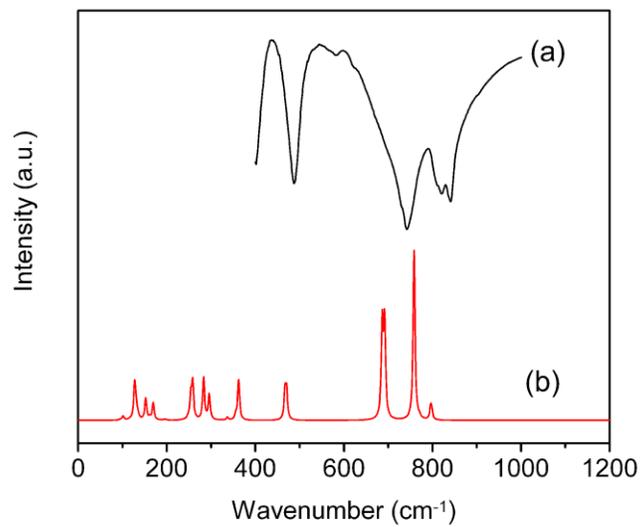


Figure S3. (a) Experimental and (b) calculated IR spectra of the BaGeO₃ crystal.

Table S3. Calculated Raman/IR Modes of the BaGeO₃ Crystal and Their Corresponding Frequencies

No.	Mode	ω/cm^{-1}	No.	Mode	ω/cm^{-1}	No.	ω/cm^{-1}	Mode
1	*B _u	-0.02	31	B _g	151.24	61	A _u	337.01
2	*A _u	-0.02	32	B _u	151.57	62	B _g	338.07
3	*B _u	-0.01	33	A _g	160.16	63	A _g	354.59
4	A _u	63.53	34	B _u	161.49	64	B _u	355.78
5	B _u	63.78	35	B _u	169.17	65	B _u	362.12
6	B _g	87.28	36	B _g	183.28	66	B _g	395.92
7	A _u	88.60	37	B _u	194.42	67	A _u	443.34
8	B _u	89.53	38	A _g	195.83	68	A _g	446.19
9	A _g	89.95	39	A _u	197.41	69	A _g	465.13
10	B _u	93.41	40	B _g	201.72	70	B _u	466.62
11	B _g	93.85	41	A _u	235.36	71	A _u	470.20
12	A _u	94.73	42	A _g	237.71	72	B _g	473.05
13	A _g	96.88	43	A _u	238.08	73	B _u	686.43
14	A _u	100.30	44	A _g	238.64	74	B _g	689.63
15	B _u	101.40	45	B _u	246.68	75	A _g	689.79
16	A _g	103.08	46	A _u	249.53	76	A _u	691.79
17	B _g	104.52	47	B _u	253.63	77	B _u	713.17
18	B _u	115.43	48	A _u	257.55	78	B _g	713.18
19	B _g	118.63	49	A _g	258.27	79	B _u	758.25
20	A _u	124.70	50	B _g	265.72	80	A _g	759.18
21	B _u	127.26	51	A _g	270.55	81	A _u	759.22
22	A _u	131.72	52	B _g	271.415	82	A _u	767.26
23	B _g	132.22	53	B _u	282.27	83	A _g	769.47
24	A _g	132.68	54	A _g	293.22	84	B _g	769.86
25	B _u	134.39	55	B _g	293.61	85	B _u	770.87
26	B _g	138.67	56	B _u	293.99	86	B _u	795.71
27	A _u	139.47	57	A _u	295.27	87	B _g	796.66
28	A _u	140.68	58	B _g	297.45	88	A _g	797.54
29	A _g	141.96	59	A _u	335.19	89	A _u	798.06
30	B _g	148.29	60	A _g	335.40	90	B _g	830.62

*Acoustic phonon

The Raman-active phonons are highlighted by red color.