Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Material: Comprehensive Raman study of orthorhombic $\kappa/\varepsilon - Ga_2O_3$ and the impact of rotational domains

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The SI contains the atomic geometry, polarized Raman spectra illustrating the allocation of experimental and calculated Raman frequencies as well as the calculated phonon dispersion of κ-Ga_2O_3.

ATOMIC GEOMETRY OF THE ORTHORHOMBIC κ-POLYMORPH

This section provides an overview of the initial and optimized geometries utilized in our calculations.

Initial geometry

The atomic positions and lattice parameter for the initial geometry were taken from Ref. 1.

Lattice vectors (in Å)
$\vec{a}_1$: 5.0463 0.0000 0.0000
$\vec{a}_2$: 0.0000 8.7021 0.0000
$\vec{a}_3$: 0.0000 0.0000 9.2833

Atomic positions of the initial geometry in coordinates of the lattice vectors, $\vec{r}=r_1\vec{a}_1 + r_2\vec{a}_2 + r_3\vec{a}_3$.

Atom	r_1	r_2	r_3
O	0.350699991	0.492300004	0.137400001
O	-0.016899999	0.494300008	-0.093400002
O	0.335599989	0.154300004	0.150399998
O	0.847599983	0.670400023	0.169400007
O	0.000899999	0.829299986	0.409399986
O	0.508099973	0.666299999	-0.097400002
O	-0.350699991	-0.492300004	0.637400001
O	0.016899999	-0.494300008	0.406599998
O	-0.335599989	-0.154300004	0.650399998
O	-0.847599983	-0.670400023	0.669400007
O	-0.000899999	-0.829299986	0.909399986
O	-0.508099973	-0.666299999	0.402599998
O	0.850699991	0.007699996	0.137400001
O	0.483100000	0.005699992	-0.093400002
O	0.835599989	0.345699996	0.150399998
O	1.347599983	-0.170400023	0.169400007
O	0.500899999	-0.329299986	0.409399986
O	1.008099973	-0.166299999	-0.097400002
O	0.149300009	0.992300004	0.637400001
O	0.516899999	0.994300008	0.406599998
O	0.164400011	0.654300004	0.650399998
O	-0.347599983	1.170400023	0.669400007
O	0.499100000	1.329299986	0.909399986
O	-0.008099973	1.166299999	0.402599998
Ga	0.183889999	0.339839995	0.027850000
Ga	0.675490022	0.530449986	0.036959998
Ga	0.189109996	0.652779996	0.250349998
Ga	0.174209997	0.652989984	-0.160760000
Ga	-0.183889999	-0.339839995	0.527850000
Ga	-0.675490022	-0.530449986	0.536959998
Ga	-0.189109996	-0.652779996	0.750349998
Ga	-0.174209997	-0.652989984	0.339239999
Ga	0.683889999	0.160160005	0.027850000
Ga	1.175490022	-0.030449986	0.036959998
Ga	0.689109996	-0.152779996	0.250349998
Ga	0.674209997	-0.152989984	-0.160760000
Ga	0.316110000	0.839839995	0.527850000
Ga	-0.175490022	1.030449986	0.536959998
Ga	0.310890004	1.152779996	0.750349998
Ga	0.325790003	1.152989984	0.339239999

Optimized geometry

Lattice vectors (in Å)
$\vec{a}_1$: 5.0283 0.0000 0.0000
$\vec{a}_2$: 0.0000 8.6209 0.0000
$\vec{a}_3$: 0.0000 0.0000 9.2114

Atomic positions of the optimized geometry in coordinates of the lattice vectors, $\vec{r}$=$r_1\vec{a}_1 + r_2\vec{a}_2 + r_3\vec{a}_3$.

Atom	r_1	r_2	r_3
O	0.348954271	0.497226135	0.136524530
O	-0.022817242	0.487498102	-0.094069859
O	0.345266653	0.158817606	0.140978434
O	0.849127984	0.671268259	0.167206320
O	-0.026463084	0.825286183	0.411794904
O	0.521691793	0.666647694	-0.099267436
O	-0.348954271	-0.497226135	0.636524530
O	0.022817242	-0.487498102	0.405930141
O	-0.345266653	-0.158817606	0.640978434
O	-0.849127984	-0.671268259	0.667206320
O	0.026463084	-0.825286183	0.911794904
O	-0.521691793	-0.666647694	0.400732564
O	0.848954271	0.002773865	0.136524530
O	0.477182758	0.012501898	-0.094069859
O	0.845266653	0.341182394	0.140978434
O	0.349127984	-0.171268259	0.167206320
O	0.473536916	-0.325286183	0.411794904
O	0.021691793	-0.166647694	-0.099267436
O	0.151045729	0.997226135	0.636524530
O	0.522817242	0.987498102	0.405930141
O	0.154733347	0.658817606	0.640978434
O	-0.349127984	0.171268259	0.667206320
O	0.526463084	0.325286183	0.911794904
O	-0.021691793	0.166647694	0.400732564
Ga	0.186596894	0.338109577	0.029961599
Ga	0.677921005	0.531046505	0.043366267
Ga	0.191108026	0.650828560	0.252211163
Ga	0.178685369	0.651661312	-0.158505938
Ga	-0.186596894	-0.338109577	0.529961599
Ga	-0.677921005	-0.531046505	0.543366267
Ga	-0.191108026	-0.650828560	0.752211163
Ga	-0.178685369	-0.651661312	0.341494062
Ga	0.686596894	0.161890423	0.029961599
Ga	0.177921005	-0.031046505	0.043366267
Ga	0.691108026	-0.150828560	0.252211163
Ga	0.678685369	-0.151661312	-0.158505938
Ga	0.313403106	0.838109577	0.529961599
Ga	-0.177921005	0.031046505	0.543366267
Ga	0.308891974	0.150828560	0.752211163
Ga	0.321314631	0.151661312	0.341494062

POLARIZED RAMAN SPECTRA

Fig. S1 illustrates the experimental Raman spectra (black lines) from Fig. 4 corresponding to the calculated (magenta lines) Raman spectra and mode intensities (magenta bars) predicted for the orthorhombic crystal structure. Raman frequencies of all experimentally determined modes are listed in Table 4 in conjunction with their theoretical counterparts.

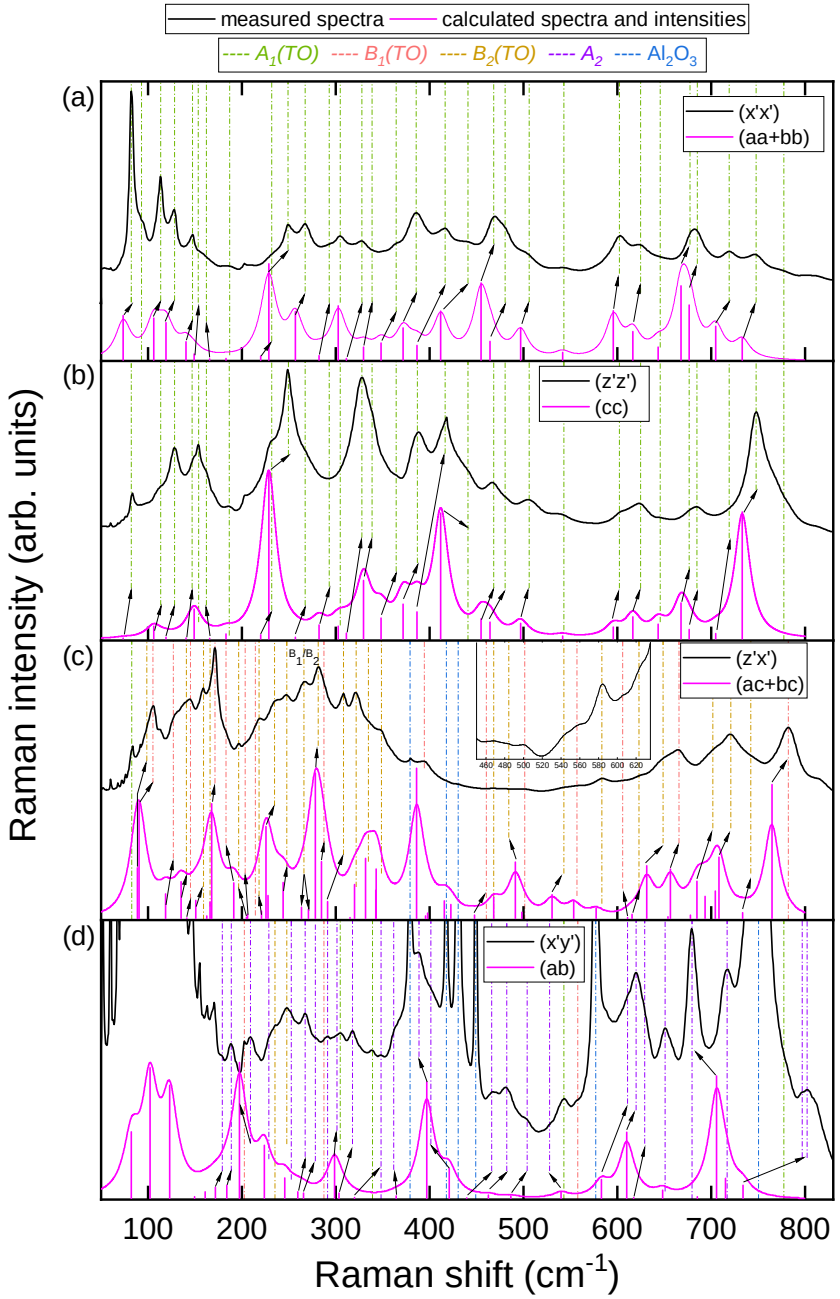

FIGURE S1. Raman spectra of the MBE-grown κ-Ga_2O_3 thin film on (0001)-oriented Al_2O_3. **a)** Raman spectra in parallel polarization for excitation on the edge. The Cartesian coordinate system x', y', z' is chosen such that z'-axis aligns with the [001] direction, with the x' and y' directions oriented according to Fig. 3. In the $y'(x'x')\bar{y}'$ configuration, the polarization vectors are aligned along the excited edge. Mode symmetries of Raman peaks associated with the κ-Ga_2O_3 thin film or sapphire substrate are indicated by vertical dashed lines. A respective line's color denotes the vibrational mode symmetry as provided on top of the graphs. Experimental modes are correlated with their calculated (magenta) counterparts. Where necessary the correlation is indicated using black arrows. **b)** Raman spectra in parallel polarization with polarization vectors aligned along the $z' \parallel c$ axis. **c)** Raman spectra of the edge in crossed polarization, with the incident or scattered light aligning with the [001] or x' directions. The inset depicts the spectrum between 450 and 640 cm^{-1} with magnified y-scale. $B_1(TO)$ and $B_2(TO)$ modes are labeled based on their correlation to the calculated Raman frequencies as explained in the text. **d)** Confocal Raman spectra in crossed polarization. The spectrum is multiplied by a constant factor to magnify low-intensity modes.

PHONON DISPERSION OF THE κ-POLYMORPH

Fig. S2 shows the calculated phonon dispersion of orthorhombic κ-Ga_2O_3 along a path between selected high symmetry points in the Brillouin zone and the phonon density-of-states (phDOS). We explicitly calculated the vibrations on a discrete grid of 6x4x4 phonon wavevectors and then obtained the phonon dispersion along the desired path through Fourier interpolation. For the phDOS, we interpolated the dispersion onto a finer discrete grid of 20x12x12 q-points and used a Gaussian broadening of the peaks with a FWHM of 0.1 cm^{-1}. We refer to the main text for the computational parameters used for the groundstate and general phonon calculations.

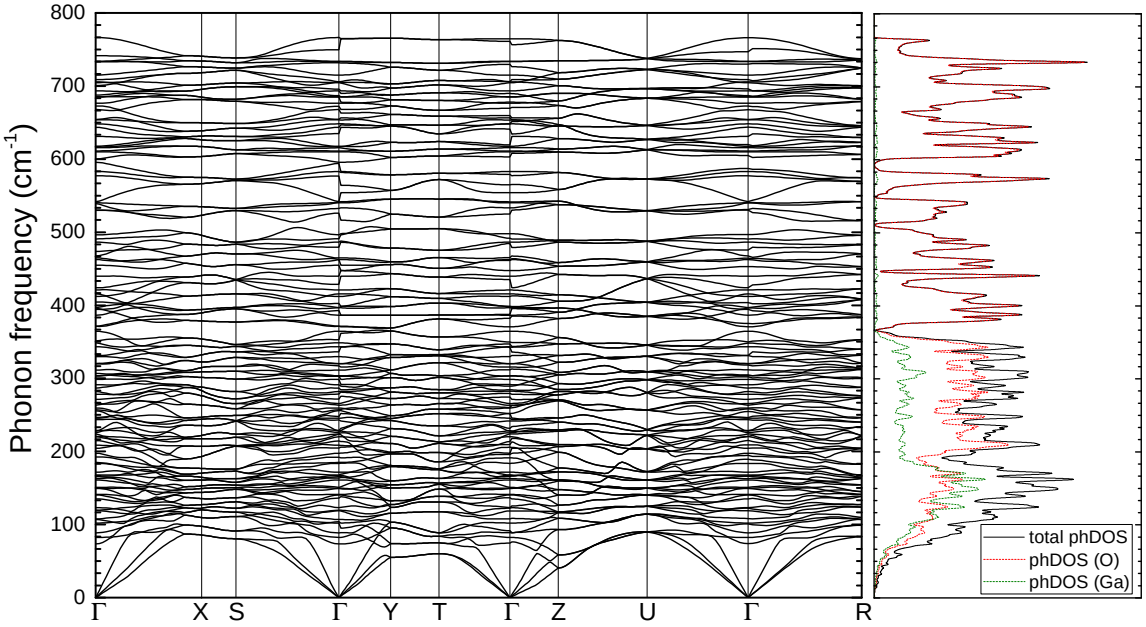

FIGURE S2. Left: Calculated phonon dispersion of κ-Ga_2O_3. The labels indicate high symmetry points with the following coordinates in terms of reciprocal lattice vectors: $\Gamma \to (0.0,0.0,0.0)$, $X \to \left(\frac{1}{2},0.0,0.0\right)$, $Y \to \left(0.0,\frac{1}{2},0.0\right)$, $Z \to \left(0.0,0.0,\frac{1}{2}\right)$, $S \to \left(\frac{1}{2},\frac{1}{2},0.0\right)$, $T \to \left(0.0,\frac{1}{2},\frac{1}{2}\right)$, $U \to \left(\frac{1}{2},0.0,\frac{1}{2}\right)$, $R \to \left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$. Right: Calculated phonon density-of-states (phDOS) and partial phDOS of the contributions of the vibrations of the O and Ga atoms. The square of the phonon eigenvectors was used a weight for the calculations of the partial phDOS for the different species.

CALCULATED RAMAN TENSOR ELEMENTS OF κ-GA_2O_3

Tables S1-S3 list the calculated Raman tensor elements used for the simulation of the Raman spectra in the main text. We refer to the method part for the employed computational procedure and parameters. The labels follow the usual convention for the Raman tensor,

$$\mathscr{R} \propto \begin{pmatrix} a & d & f \\ d & b & e \\ f & e & c \end{pmatrix}.$$

TABLE S1. Calculated Raman tensor elements (in arb.u) and frequencies ω (in cm^{-1}) of the calculated phonon modes of κ-Ga_2O_3. For the sake of readability, we followed the convention used recently in Ref. 2 and rescaled the values obtained from our DFT calculations such that the largest Raman tensor element has value 1000. The final two columns indicate the point-group symmetry of the phonon mode and whether it is (as per point-group symmetry) Raman (R) or infrared active (I).

Phonon mode	ω	a	b	c	d	e	f	Symmetry	Optical activity
1	73.5	-109	55	13	0	0	0	A_1	I+R
2	82.4	0	0	0	-47	0	0	A_2	R
3	88.8	0	0	0	0	49	0	B_2	I+R
4	90.2	0	0	0	0	0	75	B_1	I+R
5	102.1	0	0	0	-80	0	0	A_2	R
6	106.2	115	-121	69	0	0	0	A_1	I+R
7	118.7	0	0	0	0	0	-45	B_1	I+R
8	119.2	-130	-118	-28	0	0	0	A_1	I+R
9	123.2	0	0	0	-89	0	0	A_2	R
10	135.0	0	0	0	0	61	0	B_2	I+R
11	140.6	109	89	23	0	0	0	A_1	I+R
12	141.1	0	0	0	0	0	8	B_1	I+R
13	149.3	-64	-57	-144	0	0	0	A_1	I+R
14	149.7	0	0	0	11	0	0	A_2	R
15	151.0	0	0	0	0	-47	0	B_2	I+R
16	161.0	0	0	0	-26	0	0	A_2	R
17	162.5	0	0	0	0	-18	0	B_2	I+R
18	165.6	-39	1	-21	0	0	0	A_1	I+R
19	166.1	0	0	0	0	49	0	B_2	I+R
20	167.7	0	0	0	0	0	131	B_1	I+R
21	171.6	0	0	0	37	0	0	A_2	R
22	182.9	3	-49	69	0	0	0	A_1	I+R
23	183.7	0	0	0	-42	0	0	A_2	R
24	191.2	0	0	0	0	0	-81	B_1	I+R
25	197.5	0	0	0	147	0	0	A_2	R
26	204.6	0	0	0	0	-16	0	B_2	I+R
27	206.1	0	0	0	0	0	-29	B_1	I+R
28	213.6	0	0	0	0	0	4	B_1	I+R
29	220.1	-52	-78	75	0	0	0	A_1	I+R
30	221.1	0	0	0	0	-42	0	B_2	I+R
31	223.8	0	0	0	-101	0	0	A_2	R
32	225.7	0	0	0	0	150	0	B_2	I+R
33	227.6	0	0	0	0	0	-75	B_1	I+R
34	228.6	358	339	493	0	0	0	A_1	I+R
35	241.3	0	0	0	0	0	5	B_1	I+R
36	243.8	0	0	0	0	-100	0	B_2	I+R
37	245.5	0	0	0	-68	0	0	A_2	R
38	251.9	0	0	0	0	0	-10	B_1	I+R
39	257.0	-182	-338	-52	0	0	0	A_1	I+R
40	259.5	0	0	0	39	0	0	A_2	R
41	263.3	0	0	0	0	0	59	B_1	I+R
42	265.7	0	0	0	-35	0	0	A_2	R
43	270.8	0	0	0	0	-56	0	B_2	I+R
44	278.3	0	0	0	0	-223	0	B_2	I+R
45	282.0	8	122	167	0	0	0	A_1	I+R
46	284.7	0	0	0	0	0	142	B_1	I+R
47	289.3	0	0	0	0	0	-11	B_1	I+R
48	291.4	0	0	0	0	79	0	B_2	I+R
49	298.6	0	0	0	-117	0	0	A_2	R
50	302.7	-319	-336	-167	0	0	0	A_1	I+R

TABLE S2. continuation of Tab. S1.

Phonon mode	ω	a	b	c	d	e	f	Symmetry	Optical activity
51	303.4	0	0	0	39	0	0	A_2	R
52	311.4	65	-32	114	0	0	0	A_1	I+R
53	315.4	0	0	0	0	0	17	B_1	I+R
54	320.0	0	0	0	14	0	0	A_2	R
55	320.1	0	0	0	0	120	0	B_2	I+R
56	329.7	19	240	387	0	0	0	A_1	I+R
57	331.5	0	0	0	0	-164	0	B_2	I+R
58	342.7	0	0	0	0	0	-116	B_1	I+R
59	343.2	0	0	0	0	-153	0	B_2	I+R
60	348.4	267	111	240	0	0	0	A_1	I+R
61	364.5	0	0	0	31	0	0	A_2	R
62	370.4	0	0	0	0	0	3	B_1	I+R
63	371.9	-196	-367	-326	0	0	0	A_1	I+R
64	386.2	0	0	0	0	0	-292	B_1	I+R
65	386.4	-138	255	295	0	0	0	A_1	I+R
66	395.8	0	0	0	0	-40	0	B_2	I+R
67	396.8	0	0	0	235	0	0	A_2	R
68	397.9	0	0	0	0	0	-56	B_1	I+R
69	411.9	384	398	671	0	0	0	A_1	I+R
70	415.6	0	0	0	0	-105	0	B_2	I+R
71	420.8	0	0	0	-124	0	0	A_2	R
72	422.4	0	0	0	0	-95	0	B_2	I+R
73	439.6	0	0	0	12	0	0	A_2	R
74	447.6	0	0	0	0	0	-47	B_1	I+R
75	454.8	-394	-633	-286	0	0	0	A_1	I+R
76	462.6	0	0	0	43	0	0	A_2	R
77	464.3	-372	28	267	0	0	0	A_1	I+R
78	468.5	0	0	0	0	126	0	B_2	I+R
79	486.3	0	0	0	38	0	0	A_2	R
80	491.2	0	0	0	0	212	0	B_2	I+R
81	497.0	476	188	267	0	0	0	A_1	I+R
82	498.3	0	0	0	0	0	-70	B_1	I+R
83	530.5	0	0	0	0	145	0	B_2	I+R
84	533.2	0	0	0	0	0	-10	B_1	I+R
85	540.1	0	0	0	-70	0	0	A_2	R
86	541.6	-256	59	-119	0	0	0	A_1	I+R
87	553.5	0	0	0	0	0	-131	B_1	I+R
88	577.4	0	0	0	0	-102	0	B_2	I+R
89	583.0	0	0	0	-123	0	0	A_2	R
90	595.8	-409	-591	-267	0	0	0	A_1	I+R
91	610.1	0	0	0	239	0	0	A_2	R
92	610.9	0	0	0	0	0	31	B_1	I+R
93	615.6	0	0	0	0	-67	0	B_2	I+R
94	616.6	-318	-461	371	0	0	0	A_1	I+R
95	617.5	0	0	0	-24	0	0	A_2	R
96	631.2	0	0	0	0	-243	0	B_2	I+R
97	643.5	370	119	312	0	0	0	A_1	I+R
98	648.2	0	0	0	87	0	0	A_2	R
99	653.8	0	0	0	0	0	7	B_1	I+R
100	653.9	0	0	0	0	-48	0	B_2	I+R

TABLE S3. continuation of Tab. S1.

Phonon mode	ω	a	b	c	d	e	f	Symmetry	Optical activity
101	656.6	0	0	0	0	0	-241	B_1	I+R
102	667.9	-535	-788	-501	0	0	0	A_1	I+R
103	676.3	816	129	258	0	0	0	A_1	I+R
104	677.6	0	0	0	0	0	66	B_1	I+R
105	684.9	0	0	0	0	216	0	B_2	I+R
106	685.2	0	0	0	36	0	0	A_2	R
107	689.7	0	0	0	0	0	0	B_1	I+R
108	693.4	0	0	0	0	168	0	B_2	I+R
109	704.4	0	0	0	0	0	-189	B_1	I+R
110	705.0	-363	-559	-198	0	0	0	A_1	I+R
111	705.6	0	0	0	359	0	0	A_2	R
112	708.2	0	0	0	0	282	0	B_2	I+R
113	715.0	0	0	0	146	0	0	A_2	R
114	733.1	197	505	999	0	0	0	A_1	I+R
115	733.4	0	0	0	0	88	0	B_2	I+R
116	733.8	0	0	0	120	0	0	A_2	R
117	764.6	0	0	0	0	0	440	B_1	I+R

REFERENCES

1. I. Cora, F. Mezzadri, F. Boschi, M. Bosi, M. Čaplovičová, G. Calestani, I. Dódony, B. Pécz, and R. Fornari, "The real structure of ε-ga2o3 and its relation to κ-phase," CrystEngComm **19**, 1509–1516 (2017).
2. C. Kranert, C. Sturm, R. Schmidt-Grund, and M. Grundmann, "Raman tensor elements of β-ga2o3," Scientific Reports **6**, 35964 (2016).