Phase diagram and polarization of stable phases of (Ga$_{1-x}$In$_x$)$_2$O$_3$

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The full phase diagram of (Ga$_{1-x}$In$_x$)$_2$O$_3$ is obtained theoretically. The phases competing for the ground state are monoclinic $\beta$ (low $x$), hexagonal ($x \approx 0.5$), and bixbyite (large $x$). Three disconnected mixing regions interface with two distinct phase-separation regions, and at $x \approx 0.5$, the coexistence of hexagonal and $\beta$ alloys with phase-separated binary components is expected. We also explore the permanent polarization of the phases, but none of them are polar. On the other hand, we find that $\epsilon$-Ga$_2$O$_3$, which was stabilized in recent experiments, is pyroelectric with a large polarization and piezoelectric coupling, and could be used to produce high-density electron gases at interfaces.

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work,1–3) large error bars are expected from the limited configurational sampling, but as the errors should largely cancel out when the various phases are compared, we deem the relative energetics to be rather reliable.) As shown in Fig. 2, we find that the lowest-energy structures of the sample of configurations for the hex symmetry near \( x = 0.5 \) are lower in mixing free energy by about 0.1 eV than the free-standing bixbyite configurational sample, and therefore are more stable than the bixbyite alloy.

In previous work,1–3) we reported that the alloy adopting the \( \beta \) structure of \( \text{Ga}_2\text{O}_3 \) is disfavored over bixbyite for \( x \) above 0.1 or so. The internal energy of that phase increases dramatically and monotonically in that region of \( x \), so we refrained from pursuing it further. However, the same paper reporting the occurrence of hex phase crystallites also indicated \( \beta \)-phase inclusions near \( x = 0.5 \), so we revisited our previous assessment and studied the \( \beta \) phase in that region of concentration. We found that at exactly \( x = 0.5 \), the \( \beta \) phase is more stable than bixbyite and as stable as the hex phase discussed above (see Fig. 2; a similar finding was reported in Ref. 5). At this concentration, In atoms occupy all the octahedral sites, and Ga atoms occupy all the tetrahedral sites. However, consistent with our previous conclusions, as soon as we move away from an exact 50:50 concentration, the energy shoots up immediately on both sides of the \( x = 0.5 \) minimum, accompanied by a volume collapse (mainly of the tetrahedra) by over 10% at \( x = 0.47 \) and 0.53 (the energy points for the latter concentrations are far outside the frame of the figure). Therefore, the \( \beta \) phase itself should occur only at the “magic” 50:50 concentration, or near that concentration if one assumes that some other phase will take up the local cation excess.

We thus provide an improved phase diagram accounting for the new phases. The diagram is shown in Fig. 2 as the mixing free energy versus \( x \). The temperature is 800 K, a typical growth temperature. As shown previously,3) the phase boundaries are insensitive to temperature within our model and hence apply to all practical growth temperatures. That is, the miscibility gaps and miscibility regions are persistent with temperature.

The stability of the \( \beta \) phase only at low \( x \) is confirmed, and so is the phase separation into components of the bixbyite phase in most of its own range (signaled by the free energy being everywhere upward-convex), except for \( x \geq 0.9 \). What is new is that the hex phase is now the stable one in a range that, conservatively, extends from \( x \sim 0.4 \) to \( x \sim 0.6 \). Given its upward-concave (positive-curvature) free energy, the hex phase does not phase-separate into binary components in this range. In addition, as mentioned, the \( \beta \) phase has a very narrow stability slot at \( x = 0.5 \).

As dictated by the curvature of the mixing free energy, the two binary oxides are fully miscible at all temperatures in the ranges \( x \in (0, 0.18) \), \( x \in (0.4, 0.6) \), and \( x \in (0.9, 1) \), where the \( \beta \), hex, and bixbyite structures, respectively, appear. (These \( x \) values correspond to the inflection points of the mixing free energy.) In the rest of the \( x \) range, separation into binaries is expected from the convex mixing free energy.

In the central region of the \( x \) range, there are several competing possibilities. The hex and \( \beta \) mixed phases are obviously favored over the bixbyite alloy. However, the latter should phase-separate into binary components, with \( \text{In}_2\text{O}_3 \) certainly adopting the bixbyite structure. \( \text{Ga}_2\text{O}_3 \) may be either bixbyite or \( \beta \). In the first case, the energy (obtained by interpolation between the end values) is about 0.02 eV; that is, it falls between those of the \( \beta \) alloy and the hex. In the second case, the free energy is zero by construction, making phase separation at 50% slightly favored. These considerations, however, neglect internal interfaces, grain boundaries, strain effects in the binaries, and the growth kinetics (all of which are exceedingly complicated and well beyond our present scope), which will tend to disfavor phase separation. Thus, at this level of accuracy, it seems very plausible that— as experiments suggest — the hex, \( \beta \), and phase-separated binaries will coexist in this region, depending on the growth conditions.

In Fig. 3, we show the calculated fundamental gap in the stable phases in the regions where mixing occurs. The gap is calculated as the difference in the Kohn–Sham GGA eigenvalues plus the empirical correction used in Ref. 3 to adjust the gap of the binaries to the experimental values. At low \( x \) and high \( x \), one expects optical absorption typical of \( \text{Ga}_2\text{O}_3 \) and \( \text{In}_2\text{O}_3 \), respectively. Around \( x \sim 0.5 \), the hex and \( \beta \) alloy absorptions should be present. Because the bixbyite alloy phase separates, absorption may also be observed at energies typical of \( \text{Ga}_2\text{O}_3 \) (4.5–4.7 eV) and \( \text{In}_2\text{O}_3 \) (2.9 eV forbidden, 3.5 eV allowed); thus, in the central \( x \) region, distinct transitions may be expected at roughly 3.5, 4, and 4.5 eV. For the non-mixing regions, absorption at 3.5 and 4.5 eV from the two binaries should be observed.

One reason to investigate the hex phase is to check whether it distorts into a non-centrosymmetric symmetry group as a consequence of alloying. We investigate a range of alloying contents between 43 and 57%, enabling all
symmetry reductions starting from $P6_3/mmc$. We find that
the polarization is always numerically zero with respect to
the nonpolar high-symmetry phase and are thus forced to
conclude that this structure, somewhat anticlimactically,
is robustly nonpolar. In fact, our conclusion agrees with the
symmetry determination of Ref. 14 at $x = 0.5$ and shows that
this applies at generic concentrations in that vicinity. We
also sampled the polarization in a few bixbyite and $\beta$ alloy
samples and, unsurprisingly, found them to be always zero
(with respect to the cubic and monoclinic $\beta$ phases).

We therefore turned to another potentially polar phase of
this system, $\varepsilon$-$\text{Ga}_2\text{O}_3$, which was recently grown epitaxially
on GaN.7) The $\varepsilon$ phase is generally assumed$^9$ to be struc-

turally akin to the same phase of Fe$_2$O$_3$; its space group is
$Pna2_1$, which does not contain inversion. We calculated
its structural parameters and found them to be in essential
agreement with a previous study.8) The energy difference
from the $\beta$ phase at zero temperature is just 90 meV per
formula unit.

At sufficiently low temperature, the epitaxial stabilization$^7$
of the $\varepsilon$ phase is not endangered by a possible decay in the $\beta$
ground state, for the simple reason that there is no possible$^6$
$\varepsilon$-to-$\beta$ symmetry path, as the two space groups are $Pna2_1$ and
$C2/m$, respectively. This is quite analogous to the situation
of wurtzite III-V nitrides (group $P6\beta mc$), which cannot transform,
again for symmetry reasons, into the closely related structure of zincblende (group $F4\overline{3}m$), although the volumes are almost the same and the energy difference
is only about 10 meV/atom (the two $\varepsilon$ and $\beta$ phases also
have the same volume and an energy difference of about
15 meV/atom). Just like $\varepsilon$-$\text{Ga}_2\text{O}_3$, zincblende nitrides can be
grown under appropriate epitaxial constraints.

Because the group $Pna2_1$ does not contain inversion,
observable polar vector quantities are allowed in $\varepsilon$-$\text{Ga}_2\text{O}_3$.
The polar axis is the $c$-axis, so we calculate the spontaneous
polarization $P = (0, 0, P)$ as the difference between the polarizations calculated$^{10}$ in this phase and in a symmetry-
connected centrosymmetric parent phase (we verified that the
other components are indeed zero). The latter is chosen to
have symmetry group $Pma$ (a supergroup of $Pna2_1$). The
evolution of $P$ with a path connecting the two structures is
shown in Fig. 4.

The final result is that $\varepsilon$-$\text{Ga}_2\text{O}_3$ has a remarkable $P$ value of
0.23 C/m$^2$, which is similar to that of BaTiO$_3$, a factor of 3
larger than that of AlN, and nearly a factor of 10 larger than
that of GaN. The structure of the $\varepsilon$ phase is not structurally
switchable (in the same sense that wurtzite is not, though of

course the polar axis can be inverted, again as in nitrides, by
inverting the growth direction using, e.g., a buffer layer). Therefore, $P$ is expected to maintain its orientation along
the polar axis within any given crystalline domain. $\varepsilon$-$\text{Ga}_2\text{O}_3$
can thus be classified as a pyroelectric material, another
resemblance to III-V nitrides. The symmetry of the $\varepsilon$-$\text{Ga}_2\text{O}_3$
structure allows for five distinct piezoelectric coefficients; here we calculate the diagonal coefficient $\varepsilon_{33}$ as the finite-
differences derivative of the polarization with respect to the
axial strain, $\varepsilon_3 = (c - c_0)/c_0$. The result, $\varepsilon_{33} = 0.77$ C/m$^2$,
is in line with typical coefficients of strongly polar semicon-
ductors (oxides and nitrides), although it is more than an
order of magnitude smaller than those of strong ferro-
electrics.$^{15}$

We briefly comment on the structural assessment of the $\varepsilon$ phase, although it is beyond our present scope. The GaN-
epitaxial Ga$_2$O$_3$ phase is reportedly$^7$ hexagonal $P6\beta mc$ (no
detailed structural information is available); a recent study$^{16}$
suggested a bulk structure of the same symmetry charac-
terized by disordered Ga vacancies, admixed with the $\beta$ phase.
Such a structure cannot be compared theoretically with our
$Pna2_1$ structure owing to disorder and phase mixing. Further,
any such structure will still exhibit spontaneous polarization
because $P6\beta mc$ is also a polar group. Indeed, calculations for
a highly simplified structure mimicking that suggested by
experiments$^6$ give a $P$ value similar to that of $Pna2_1$.

More generally, the structure we adopt here is still a
relevant candidate, as the orthorhombic $Pna2_1$ and hexagonal
$P6\beta mc$ structures can be transformed into one another by
local distortions ($Pna2_1$ is a subgroup of $P6\beta mc$, and a polar-
axis view of the Ga sites in our structure clearly shows a
distorted hexagonal pattern). Epitaxy on GaN may force
Ga$_2$O$_3$ into a $P6\beta mc$ structure closely related to $Pna2_1$, as
Ga$_2$O$_3$ is known to adapt fairly

distorted hexagonal pattern. Epitaxy on GaN may force
Ga$_2$O$_3$ into a $P6\beta mc$ structure closely related to $Pna2_1$, as
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antiparallel. Because the polarization difference is very large in both cases, a correspondingly large polarization charge will appear at the GaN/$\varepsilon$-Ga$_2$O$_3$ interface and thus attract free carriers (e.g., provided by dopants) to form an interface-localized two-dimensional gas at potentially huge concentrations. The polarization difference across the interface, that is, the polarization charge to be screened by free carriers, and hence the potentially reachable local electron gas concentration, is 0.2 to 0.26 C/m$^2$, that is, 1.2 to 1.6 x 10$^{14}$ cm$^{-2}$ (for parallel or antiparallel $\mathbf{P}$ vectors in the two materials, and neglecting possible interface traps, native charges, and so on). In addition, because the gap in $\varepsilon$-Ga$_2$O$_3$ is much larger than that in GaN, interface confinement should be quite efficient. Finally, the sign of the polarization charge and hence of the accumulation layer will depend on the chosen polarity of the substrate. The above scenario is a “writ-large” version of the GaN/AlGaN high-electron-mobility transistors currently in use, high-frequency, high-power operation of which is enabled primarily by the high polarization-induced interface charge. Of course, if all else is assumed to be equal, Ga$_2$O$_3$/GaN transistors could be greatly superior to AlGaN/GaN ones, which enjoy a much lower areal density on the order of 10$^{13}$ cm$^{-2}$.

In summary, we revised and extended the phase diagram of (Ga$_{1−x}$In$_x$)$_2$O$_3$, showing the following: the $\beta$ phase is stable (without phase separation into binary components) at low $x$ and exactly at a 50:50 concentration; a new hexagonal phase is stable (again without phase separation into binary components) for $x$ from about 0.4 to 0.6, where it is robustly nonpolar; and bixbyite will be favored for $x$ between 0.2 and 0.4 and above 0.6, but should phase-separate into binary components except at $x > 0.9$. Around $x \approx 0.5$, the hex, $\beta$, and phase-separated binary bixbyites should be in close competition. Optical signatures are expected at around 4.6 eV at low $x$ ($\beta$ phase), around 3.5 eV at large $x$ (bixbyite), and at 3.5, 4, and 4.5 eV from the competing phases at $x \approx 0.5$.

We further studied the $\varepsilon$-phase of Ga$_2$O$_3$ and confirmed it as the second most stable structure after $\beta$-Ga$_2$O$_3$. We found it to have a large spontaneous polarization (0.23 C/m$^2$) and a sizable diagonal piezoelectric coefficient ($\varepsilon_{13} = 0.77$ C/m$^2$). Symmetry dictates that this phase, once epitaxially stabilized, will not transform back into the ground-state $\beta$, despite having the same volume and a small energy difference; in this sense, the $\varepsilon$–$\beta$ relation is similar to that between zincblende and wurtzite III–V nitrides.

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