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Mechanism and microstructures in Ga₂O₃ pseudomartensitic solid phase transition[†]

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Solid-to-solid phase transition, although widely exploited in making new materials, challenges persistently our current theory for predicting its complex kinetics and rich microstructures in transition. The Ga₂O₃ α - β phase transformation represents such a common but complex reaction with marked change in cation coordination and crystal density, which was known to yield either amorphous or crystalline products under different synthetic conditions. Here we, via recently developed stochastic surface walking (SSW) method, resolve for the first time the atomistic mechanism of Ga₂O₃ α - β phase transformation, the pathway of which turns out to be the first reaction pathway ever determined for a new type of diffusionless solid phase transition, namely, pseudomartensitic phase transition. We demonstrate that the sensitivity of product crystallinity is caused by its multi-step, multi-type reaction pathway, which bypasses seven intermediate phases and involves all types of elementary solid phase transition steps, i.e. the shearing of O layers (martensitic type), the local diffusion of Ga atoms (reconstructive type) and the significant lattice dilation (dilation type). While the migration of Ga atoms across the close-packed O layers is the rate-determining step and yields "amorphous-like" high energy intermediates, the shearing of O layers contributes to the formation of coherent biphase junctions and the presence of a crystallographic orientation relation, $(001)_{\alpha}/(20\overline{1})_{\beta} + [120]_{\alpha}/(1\overline{3}2]_{\beta}$. Our experiment using high-resolution transmission electron microscopy further confirms the theoretical predictions on the atomic structure of biphase junction and the formation of $(20\overline{1})_{B}$ twin, and also discovers the late occurrence of lattice expansion in the nascent β phase that grows out from the parent α phase. By distinguishing pseudomartensitic transition from other types of mechanisms, we propose general rules to predict the product crystallinity of solid phase transition. The new knowledge on the kinetics of pseudomartensitic transition complements the theory of diffusionless solid phase transition.

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1. Introduction

Gallium oxide (Ga₂O₃) is an important functional material with many possible crystal structures, *e.g.* α , β , γ , δ and ε polymorphs,¹ where Ga cations can exist both in tetrahedral (GaO₄) and octahedral (GaO₆) coordinations. The structure varieties of Ga₂O₃ have led to its rich physicochemical properties and wide applications in different fields, including catalysts,² gas sensing,^{3,4} solar energy conversion devices,^{5–7} and optoelectronic devices.^{8–10} Among the phases, β -Ga₂O₃ (monoclinic, *C2/m*, #12, density 5.94 g cm⁻³) is the most stable form with half tetrahedral and half octahedral Ga ions. It can transform to the high density phase α -Ga₂O₃ (hexagonal, $R\bar{3}C$, #167, density 6.48 g cm⁻³) that has only octahedral Ga ions by elevating the pressure to ~ 6.5 GPa,¹¹ whereas the reverse α -to- β transformation can be achieved by heating (600 °C)¹ (see Fig. 1a). Compared to molecular reactions, our current understandings on the solid-to-solid reaction are however much poorer, not least because of the lack of tools to identify how atoms move in solid phase transition. For Ga₂O₃ α - β phase transition, in particular, where a large density change occurs together with a marked local coordination variation (GaO₆ to GaO₄), it has been frustrated to classify the type of such complex solid-to-solid transitions, not even to rationalize or predict the reaction kinetics.

Because the Ga₂O₃ α - β phase transition is bi-directional, both high pressure and high temperature experiments were conducted in the last twenty years and important results on the transition kinetics have been obtained. For β -Ga₂O₃ to α -Ga₂O₃ transition under high pressure at room temperature, Machon *et al.*¹² found obvious structural disordering by inspecting the

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[†] Electronic supplementary information (ESI) available: The SSW crystal pathway sampling method and the calculation detail; the experimental procedure to synthesize biphase crystals and the experimental data (XRD, SEM, TEM/HRTEM) for characterizing the biphase crystals; the biphase junction structures constructed and optimized by DFT; the atomic XYZ positions for all the states along the pathway. See DOI: 10.1039/c6cp03673b



Fig. 1 (a) α -Ga₂O₃ and β -Ga₂O₃ crystals (Bravais lattice). Ga atom: green ball; O atom: red ball. (b and c) High resolution SEM images of α -Ga₂O₃ (b) and β -Ga₂O₃ (c) nanoparticles synthesized according to the method reported by Qian *et al.*,¹⁵ in which β -Ga₂O₃ is obtained *via* the solid phase transition of α -Ga₂O₃.

structure evolution during phase transition, which is evident from the broadening of peaks in the in situ high-resolution synchrotron X-ray diffraction (XRD) patterns and the in situ Raman spectrum. By contrast, the thermally activated phase transition from α -Ga₂O₃ to β -Ga₂O₃ is able to produce wellcrystallized β-phase, which can be synthesized from GaOOH precursor.^{13,14} In the phase transition, the morphology of β -Ga₂O₃ can often be preserved as that of GaOOH or α -Ga₂O₃ without particle aggregation and fusion¹⁵ (also see Fig. 1b). Recently, Li group¹⁶ showed that the mixed phase Ga₂O₃ as the product of the partial phase transition exhibits higher photoactivity towards water splitting than individual pure phases, which was attributed to the presence of structurally ordered biphase junction as shown from HRTEM. However, the later theoretical studies¹⁷ found a large strain and atomic misfit at the phase junction between α -Ga₂O₃ and β -Ga₂O₃ using HRTEM assignment, *i.e.* (110) of α -phase parallel to ($\overline{3}10$) of β -phase, from density functional theory (DFT) calculations. While a structurally disordered phase junction from calculations may explain the disordered intermediates from high-pressure experiment, it is difficult to rationalize the higher photoactivity of mixed phase oxides since the coherent interface is believed to be a must to enhance photon-generated charges to migrate across phase boundaries.

In fact, the difficulty to understand Ga_2O_3 phase transition could be attributed to the lack of atomic level pathway of complex solid-tosolid reactions in general. For Ga_2O_3 phase transition, it involves much larger volume change (9%) than most encountered solid-tosolid reactions that can be classified as martensitic diffusionless transition, *e.g.* metal bcc–fcc transition^{18,19} and ZrO₂ t–m phase transition.^{20–22} In addition, it requires significant local atom displacement in order to change the Ga coordination. While it may be considered as a diffusional transition or a reconstructive solid-to-solid transition, the observed rapid transition kinetics¹ and the presence of structurally ordered bi-phase interface¹⁶ again question such a classification. Nevertheless, we note that the α - β Ga₂O₃ phase transition may be analogy with the well-known olivine to spinel phase transition of (Fe,Mg)₂SiO₄, which has a similar magnitude of density change (~10%) and is believed to be the origin for the deep-focus earthquakes.²³⁻²⁵ Despite its importance in nature, the olivine to spinel transition has been debated on its mechanism for the past 50 years²³⁻²⁸ and it was termed by Chen *et al.*²⁶ as a pseudomartensitic transition until recent years. The pseudomartensitic transition has a hybrid mechanism by definition, involving both displacive (martensitic) sublattice transition (anions) and atomic diffusion (cations). To date, the atomic level mechanism and kinetics on pseudomartensitic transition remains, however, largely elusive. In particular, no reaction pathway is known for a single reaction of this type.

In this work, we combine theory and experiment to resolve the mechanism and kinetics in $Ga_2O_3 \alpha - \beta$ phase transition. A novel solid reaction pathway sampling method, namely Stochastic surface walking (SSW) pathway sampling,²⁹⁻³¹ is utilized to identify the lowest energy pathway and the HRTEM technique is applied to directly observe the atomic structure at the α - β bi-phase junction. We demonstrate that the α - β Ga₂O₃ phase transition belongs to a pseudomartensitic phase transition, featuring the collective shearing of O close-packed layers and the Ga cation short-range migration across the O close-packing layer. This reaction pathway represents the first atomic level pathway ever determined for pseudomartensitic phase transition. The atomic model for pseudomartensitic phase transition established here helps to bridge the gap between different types of solid phase transition reactions, and also the gap between molecular reactions and solid phase transition reactions, which is thus of general significance in chemistry and material science.

2. Theoretical and experimental methods

2.1 Reaction pathway sampling based on SSW method

In order to explore the potential energy surface (PES) of the Ga_2O_3 phase transition, we have first utilized recently developed SSW method as integrated with first principles DFT calculations to sample the solid reaction pathways, exhaustively and unbiasedly. Here we outline the SSW pathway sampling method briefly. The SSW reaction pathway sampling is based on SSW global optimization method (see our previous work for detailed methodology of SSW²⁹⁻³¹). The SSW method is able to explore complex PES to identify unexpected new structures and at the mean time to collect the reaction pathways leading to them. For solid phase transitions, this is to identify the one-to-one correspondence for lattice $(L(e_1,e_2,e_3))$, e_i being the lattice vector) and atom $(q_i, i = 1, ..., 3N, N \text{ is the number of atom in cell})$ from one crystal phase (the initial state, IS) to another (the final state, FS), which constitutes the reaction coordinates of the reaction, *i.e.* $Q_{IS}(L,q) \rightarrow Q_{FS}(L,q)$. In one SSW pathway sampling simulation, we need to collect as many as possible such IS/FS pairs (typically a few hundreds) to ensure the identification of the best reaction coordinate, the one corresponding to the lowest

energy pathway. With such a pair of reaction coordinates, $Q_{Is}(L,q)$ and $Q_{FS}(L,q)$, it is then possible to utilize variable-cell double-ended surface walking (VC-DESW)³² method to identify the reaction transition state (TS) and the minimum energy pathway.

In our implementation, the SSW pathway sampling is fully automated and divided into three stages in simulation, namely, (i) pathway collection *via* extensive SSW global search; (ii) pathway screening *via* fast DESW pathway building;^{32–34} (iii) lowest energy pathway determination *via* DESW TS search. The first stage is the most important and most time-consuming part, which generates all the likely pairs of generalized reaction coordinates linking different crystal phases. For the α – β Ga₂O₃ phase transition in this work, we have collected more than 1000 pairs Q_{α}(L,q) and Q_{β}(L,q), which leads to the finding of the lowest energy pathway. More detail on the SSW pathway sampling are described in ESI[†] and also in our previous works.^{35–39}

It should be mentioned that the high computational cost of the SSW pathway sampling at the DFT level prevents practically the automated identification of the lowest reaction pathway for large systems (*e.g.* above 50 atoms). In this work, we utilized 10-atom ($2Ga_2O_3$ per cell) and 20-atom supercells of Ga_2O_3 crystal in the SSW pathway sampling. The lowest energy pathway obtained from sampling was then analyzed to identify the key atom displacement patterns. Using the information, we further enlarged the supercell up to 60-atom per cell and re-searched the lowest energy pathway, which is found to lower dramatically the overall reaction barrier. This is described in more detail in Section 3.1.

2.2 DFT calculation details

All calculations were performed using the plane wave DFT program, Vienna *ab initio* simulation package (VASP)⁴⁰ where the electron-ion interaction of Ga and O atoms were represented by the projector augmented wave⁴¹ (PAW) scheme and the exchange-correlation functional utilized was GGA-PBE.⁴² In the SSW pathway sampling, we adopt the following setups to speed up the PES exploration: the kinetic energy plane wave cutoff 400 eV; the Monkhorst-Pack k-point mesh of $(4 \times 4 \times 4)$ set for 10-atom supercell; 3-electron (4s²4p¹ configuration) PAW pesudopotential for Ga. All the low energy pathways have then been converged using more accurate calculation setups, i.e. the planewave cutoff 600 eV, Monkhorst–Pack k-point mesh $(8 \times 8 \times 8)$ for 10-atom supercell and $(2 \times 2 \times 2)$ for 60-atom supercell, and the semi-core included (3d¹⁰4s²4p¹) PAW pseudopotential for Ga. For all the structures, both lattice and atomic positions were fully optimized until the maximal stress component is below 0.1 GPa and the maximal force component below 0.01 eV $Å^{-1}$.

2.3 Synthesis and characterization of Ga₂O₃

We have synthesized α -Ga₂O₃, β -Ga₂O₃ and mixed phase α -Ga₂O₃/ β -Ga₂O₃ materials starting from the GaOOH precursor.^{2,15,40} The hydrothermal method was used to prepare GaOOH nanorods.¹³ In a typical synthesis, 0.1368 g Ga(NO₃)₃ was added to 75 ml deionized water, which was stirred for 1 h and 0.0970 g urea was then added to the transparency solution for another 1 h stirring. The mixed solution was poured into a 100 ml Teflon-lined

stainless steel autoclave that was placed in an oven at 125 °C for 8 h. The autoclave was then cooled to room temperature in air. The precipitates were filtered and repeatedly washed by distilled water for three times, and then dried at 80 °C overnight. After GaOOH nanorods were obtained, different phases of Ga₂O₃ were prepared by calcinating GaOOH at high temperature. The pure α -Ga₂O₃ sample was obtained by heating GaOOH at 400 °C for 2 h in air. The α -Ga₂O₃/ β -Ga₂O₃ mixed phase bicrystalline materials with different ratios were obtained by further calcinating α -Ga₂O₃ sample at 590, 610, 630, 650 °C for 2 h. The pure β -Ga₂O₃ sample can be obtained by calcination at 720 °C for 5 h.

The samples have been characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer), Field Emission scanning electron microscopy (FESEM, FEI Nova NanoSEM450, USA, operated at 2–5 kV), high resolution TEM (HRTEM, FEI Tecnai G2F20 S-Twin, USA, operated at 200 kV). XRD measurements were conducted using Cu K α radiation at a scanning rate of 7° per min in the range of 10–80°.

The identity of α -Ga₂O₃ phase in GaOOH can be verified by XRD, where the new peaks appear at 24.6° and 35.9° and the original peaks of GaOOH at 18.0°, 21.5°, 26.8°, 33.8° and 37.3° disappear (see Fig. S1 in ESI†). For β -Ga₂O₃ as synthesized from α -Ga₂O₃ by calcination, the characteristic peaks in XRD are at 30°, 32°, 35°. The phase transformation progresses with the rise of calcination temperature and completes at 720 °C with all the diffraction peaks belonging to β -Ga₂O₃. The SEM images of typical Ga₂O₃ nanostructures are shown in Fig. S2 (ESI†), which are uniform nanorods with ~3 µm in length and 500 nm in width. There are pores on α -Ga₂O₃ and β -Ga₂O₃ surfaces due to the dehydration of GaOOH.¹⁵ The HRTEM of the biphase junction will be presented in Section 3.3.

3. Results

3.1 Geometrical features of α -Ga₂O₃ and β -Ga₂O₃ crystals

Before we present our results on the reaction pathway from α -Ga₂O₃ to β -Ga₂O₃, it is worthwhile to refresh our knowledge on the atom positions and the characteristic crystallographic planes of the two phases. α -Ga₂O₃ phase (hexagonal, #167) has the same crystal structure (corundum) as the common α -Al₂O₃. The Bravais lattice of α -Ga₂O₃ contains 30 atoms (6Ga₂O₃). The oxygen anions nearly form a distorted hexagonal close-packing (hcp) structure with Ga cations filling two-thirds of the octahedra interstices. We have shown the top views of two close-packed O layers (001)_{α} in Fig. 2 (top panel), which highlights the smallest unit cell (yellow colored) and the hollow hexagon pattern of Ga atoms (blue atoms) on (001)_{α}.

Compared to α -Ga₂O₃ phase, the crystal structure of β -Ga₂O₃ (monoclinic, #12) has less symmetry and contains both tetrahedral and octahedral Ga cations. The Bravais lattice of β -Ga₂O₃ contains 20 atoms (4Ga₂O₃). The oxygen anions are in a face centered close-packing (fcc) arrangement with the close-packed plane being (201)_{β}. The top views of two neighboring closepacked O layers of (201)_{β} are also shown in Fig. 2 (bottom panel)



Fig. 2 The atom positions on the close-packed layers $(001)_{\alpha}$ and $(20\overline{1})_{\beta}$ of α -Ga₂O₃ and β -Ga₂O₃ phases. For each phase, the top views of two neighboring layers, as indicated by the blue box in the side view, are shown. The red arrows indicate a pair of Ga atoms that undergo local diffusion in the phase transition from α -Ga₂O₃ to β -Ga₂O₃ (see Section 3.2).

to compare with those of α -phase. The smallest unit cell (yellow colored) of $(20\bar{1})_{\beta}$ plane is a long parallelogram with the two edges along [010] and [1 $\bar{1}2$] ([uvw]) directions. Importantly, Ga atoms of β -Ga₂O₃ in between the close-packed O layers are not in a hexagonal pattern as that of O atoms, but form different parallelograms.

3.2 Reaction pathway

The identification of the solid-to-solid phase transition pathway has been an outstanding challenge in theory. The α -Ga₂O₃ to β -Ga₂O₃ transition represents such a complex problem with many degrees of freedom, since the pathway linking two crystal phases contains at least 10 atoms (2Ga2O3) together with six lattice parameters, in total 33 degrees of freedom (10-atom unit cell is the primitive cell for both phases). Furthermore, due to the artificial periodic constraint of crystal unit cell, the lowest energy pathway in small unit cells may still not be enough to capture the atom movement that occurs in reality. On the other hand, for the exponential increase of PES complexity with the increase of atom numbers, it remains practically impossible to search for reaction pathways in large unit cells (e.g. more than 50 atoms) using first principles based global optimization. A compromise has to be taken to identify the lowest energy pathway that is physically meaningful. In this work we took a two-step procedure, as outlined below, to resolve the pathway of α - β phase transition.

First step: DFT based SSW pathway sampling was applied to search the PES of small unit cell Ga_2O_3 crystals, including 10-atom and 20-atom unit cells, which collects all likely low energy pathways and identifies the lowest energy pathway. The utilization of small unit cells greatly expedites the first principles PES exploration and helps to identify the essential pathway information. Second step: based on the lowest energy pathway obtained from small unit cell simulation, we can learn the crystallographic orientation relation (OR) and atom displacement patterns of the transition. We then constructed manually the reaction coordinate between two phases in large unit cells up to 60 atoms, and finally determined the lowest energy pathway therein. The reaction barrier (per formula unit, f.u.) obtained in large unit cells is found to be lower than that in small unit cells, which is due to the relaxation of the periodic constraint.

a. Crystallographic orientation relationship (OR). The potential energy profiles of the lowest energy reaction pathways in a 10-atom unit cell and a 60-atom unit cell are shown in Fig. 3a. As shown, α phase is less stable than β phase by 0.19 eV per f.u. from DFT, which is consistent with the fact that β phase is most stable at ambient conditions while α phase is the high pressure phase. The 60-atom pathway has a significant lower overall barrier (0.43 eV per f.u.) compared to that of the 10-atom pathway to understand the solid phase transition process, the 10-atom pathway will also be described briefly as it demonstrates the key roles of the O sublattice shearing in the phase transition.

10-atom pathway: the lowest energy pathway in the 10-atom unit cell links two crystal phases *via* two triclinic lattices, *i.e.* α phase, a = 5.06 Å, b = 5.06 Å, c = 5.40 Å, $\alpha = 90.010^{\circ}$, $\beta = 62.05^{\circ}$, $\gamma = 120.00^{\circ}$; β phase a = 3.09 Å, b = 7.64 Å, c = 6.41 Å, $\alpha = 55.53^{\circ}$, $\beta = 76.08^{\circ}$, $\gamma = 101.63^{\circ}$. Both lattices are not the primitive cells of the phases. The SSW pathway sampling is able to explore the crystal PES by varying the lattice structures of phase, which is essential for identifying the lowest energy pathway. The reaction is a two-step reaction with a high reaction barrier, 0.97 eV per f.u., which is apparently due to the significant lattice distortion in the pathway.

One major finding from this lowest energy pathway is the presence of a simple OR between two phases as dictated by the



Fig. 3 (a) Potential energy profile for the lowest energy pathways from α -Ga₂O₃ to β -Ga₂O₃ in 10-atom and 60-atom unit cells. (b and c) The structures of α -Ga₂O₃ and β -Ga₂O₃ showing the atom correspondence and the crystallographic OR from 10-atom pathway (b) and from 60-atom pathway (c). The O atoms (red balls) in the blue circles and in the green triangles indicate two crystal plane edges that are highlighted for tracking the atom displacement patterns from α -Ga₂O₃ to β -Ga₂O₃.

O sublattices, *i.e.* hcp in α phase and fcc in β phase. The presence of OR was known to be an important feature of martensitic phase transition,^{20,36} where the phase transition involves collective shearing of crystal planes and the new phase grows layer-by-layer from the old phase. In the Ga₂O₃ phase transition, we found that the close-packed O plane (001) of α phase evolves into the close-packed O plane (201) of β -phase, which can be summarized as an OR:

$$(001)_{\alpha}//(20\bar{1})_{\beta}$$
 and $[120]_{\alpha}//[1\bar{3}2]_{\beta}$,

 $[120]_{\alpha}$ and $[1\bar{3}2]_{\beta}$ are the [uvw] directions along the close-packed O rows on the two close-packed planes, which are also parallel with each other in the phase transition. This OR may alternatively be written in the notation of O sublattice as:

 $(0001)_{hcp}//(111)_{fcc}$ and $[11\overline{2}0]_{hcp}//[1\overline{1}0]_{fcc}$

where hcp and fcc indicate the O sublattice hereafter. The sublattice and O atom correspondence between two phases can be seen clearly from Fig. 3b, where the O close-packed plane edge is indicated by blue circles. Based on the atom correspondence in the pathway, we can also track the evolution of other O planes. For example, the $(1\bar{1}0)_{hcp}$ plane of α phase in

O sublattice as indicated by the green triangles becomes the $(11\bar{3})_{fcc}$ plane of β phase in O sublattice.

60-atom pathway: the 60-atom pathway has the same OR as the 10-atom pathway, but with a large unit cell, it is possible to lower the barrier of reaction. In the lowest energy pathway, a triclinic lattice of α -Ga₂O₃ (a = 9.53 Å, b = 8.76 Å, c = 8.76 Å, α = 59.99°, β = 81.23°, γ = 72.22°) transforms to a similar lattice of β -Ga₂O₃ (a = 9.65 Å, b = 8.80 Å, c = 8.80 Å, $\alpha = 63.45^{\circ}$, $\beta =$ 82.29°, $\gamma = 91.94^{\circ}$). Obviously, the two lattice resemble with each other, and the major difference between two lattices occurs in the γ angle (by 19.7°), which is the dihedral angle in between the $(0001)_{hcp}$ and $(\bar{2}201)_{hcp}$ in α phase and in between the $(111)_{fcc}$ and $(\bar{4}\bar{4}7)_{fcc}$ planes in β phase (Fig. 3c). The pathway has multiple elementary steps with seven metastable intermediates, indexed from MS-A to MS-G in Fig. 4. The pathway in the large unit cell becomes significantly more complex than the pathway identified in the 10-atom unit cell. This is mainly caused by complex patterns of Ga cation local movement in the phase transition, as will be discussed below.

We may understand the much lower barrier of the 60-atom pathway as follows. For the solid phase transition, the OR cannot determine the atom displacement pattern by itself. In the simplest scenario, the atoms in crystal can translate along one predefined lattice vectors by any integer length, which will recover the whole crystal structure and thus does not affect the OR. The 10-atom pathway and 60-atom pathway, although share the same OR, differ in the detailed atom displacement patterns. This is evident by comparing the transformation of the O rows as indicated by the green triangles in Fig. 3b and c. In the 10-atom pathway, the O rows on $(1\overline{1}0)_{hcp}$ evolves into those on $(11\overline{3})_{fcc}$ plane. By contrast, in the 60-atom pathway, the same O rows on $(1\overline{1}0)_{hep}$ (also $(2\overline{1}0)_{\alpha}$) becomes those on $(11\overline{1})_{fcc}$ (also $(3\overline{1}0)_{\beta}$, 29.5° from $(11\overline{3})_{fcc}$ plane), indicating different atom displacement patterns in two pathways. Obviously, this subtle difference is caused by different periodic boundary conditions in different unit cells while keeping the same OR constraint. The small unit cell has a shorter periodicity and would enforce the O rows closer in space (as their images) to displace in the same pattern.

b. Atom displacement pattern and simulated XRD. Now we can inspect state-by-state how atoms displace and lattice distorts in the phase transition. Fig. 4 shows the reaction snapshots of all the intermediates (MS-A to MS-G) along the lowest energy pathway in 60-atom unit cell. To distinguish these states, we have indicated the rough symmetry of their O sublattice (measured with a large symmetry tolerance, 0.9 Å) and also the number of Ga atoms with different coordination per unit cell. It turns out that all the intermediates have either hcp or fcc lattice for the O sublattice. In addition, unusual five-coordinated Ga atoms (GaO_5) appear during the phase transition. This information has been summarized for each state in the figure. Taking the notation (fcc; [12:0:12]) of β phase as an example, it stands for the fcc-type O sublattice with 12 GaO₆, zero GaO₅ and 12 GaO₄ coordination. Also shown in Fig. 4 are the simulated the XRD patterns for the states at a radiation wavelength of 0.7 Å (a typical wavelength in synchrotron radiation), which are plotted by separating the contribution caused by the O sublattice (red lines) or the Ga sublattice (blue lines).



Fig. 4 The snapshots of reaction intermediate states along the lowest energy pathway (60-atom unit cell) and the simulated XRD spectra contributed from the O sublattice (red lines) and the Ga sublattice (blue lines). All states are viewed down from $[120]_{\alpha}$ ($(1\overline{3}2]_{\beta}$) direction. For each state, both the all atom representation (left) and the O sublattice (right) are shown. The four close-packed O layers in one unit cell (dotted line) are indexed by number from 1 to 4. O: red balls; six-coordinated Ga (GaO₆): green balls; five-coordinated Ga (GaO₅): purple balls; four-coordinated Ga (GaO₄): light-blue balls.

O sublattice displacement: on going from α phase to β phase, the O sublattice switches alternatively in between hcp and fcc structure, *i.e.* hcp \rightarrow fcc \rightarrow hcp \rightarrow fcc, which are caused by the shearing of the close-packed layers at the $[\bar{1}100]_{hcp}$ (or $[11\bar{2}]_{fcc}$) direction. The first hcp-to-fcc transition occurs at MS-A-to-MS-B; the fcc lattice transforms back to the hcp lattice at MS-F-to-MS-G; and the final hcp-to-fcc transformation occurs at MS-G-to-β phase. The simulated XRD pattern from O sublattice in Fig. 4 also shows clearly that the O sublattice retains generally well with sharp diffraction peaks originated from the close-packing structures. It is noticed that the reaction barriers of these three reactions involving O sublattice transformation are generally low, being all less than 0.12 eV per f.u., which are considerably lower than the overall barrier (0.43 eV per f.u.) from α to β phase. This indicates that the atomic movement dominated by O layer shearing cannot be rate determining to the transition.

Specifically, in the MS-A-to-MS-B step as seen from $[120]_{\alpha}$, the 1st O layer shears at $[\bar{1}100]_{hcp}$ but the 4th O layer shears oppositely at $[1\bar{1}00]_{hcp}$ (see the arrows in Fig. 4 MS-A). As a result, the O layer (1 $\bar{1}0$) plane in the hcp lattice transforms

to $(11\overline{1})$ in the fcc lattice (O rows in triangles in Fig. 4). The subsequent reactions from MS-B to MS-F retain the O fcc sublattice and the major difference between states is the change of local Ga atom coordination (will be discussed below). From MS-F to MS-G, the O close-packed layers shear further to restore the hcp lattice, featuring the relative displacement of the 1st and 2nd layers with respect to the 3rd and 4th O layers. In the final step from MG-G to β phase, the shearing of O layers is simply the reverse of the previous step to re-generate the fcc lattice.

Macroscopically, the phase transition *via* the shearing of atom layers will form the habit plane during phase propagation and maintain a clear crystallographic OR between phases. According to the classic phenomenological theory of martensitic transition, ^{43–47} the behavior of ideal martensitic transition can be interpreted using the concepts of the strain-invariant plane and the strain-invariant line. For the α - β transition, the former is determined to be the close-packed O layers, $(001)_{hcp}//(111)_{fcc}$ (area mismatch ~4%), and the latter is the close-packed O row, $[11\bar{2}0]_{hcp}//[1\bar{1}0]_{fcc}$ (strain only 0.46%). These values are close to the ZrO₂ tetragonal to monoclinic phase transition²⁰ that is regarded as a classic example of martensitic phase transition.

Based on these, we can conclude that the O sublattice displacement in the α - β transition of Ga₂O₃ has the typical characteristics of diffusionless martensitic transition.

Ga cation displacement: compared to the shearing movement of O anions, the displacement pattern of Ga cations in the phase transition is more complex. It involves both short-range diffusion (restructuring) of individual Ga atoms, and synchroshear of Ga layers as with O layers. We here highlight two representing elementary steps, namely, the first and the second step, which feature these two types of movements, respectively. These first two steps have a total barrier of 0.36 eV per f.u., which is already close to the overall barrier of the phase transition and thus important for understanding the kinetics.

The first step, α -phase to MS-A, has little change in the O sublattice, but involves the diffusion of two pairs of Ga atoms (per unit cell). This results in the migration of the Ga atoms across the close-packing O layer. We have shown the top and the side views of this step in Fig. 5, which highlights the event where one Ga atom (blue ball) exchanges with another Ga atom (yellow ball) at 3rd and 4th O layers. The similar Ga exchange occurs also at 1st and 2nd layers (not shown in the top views). The purpose of such Ga exchanges is to transform the Ga pattern on the O close-packed layer from hollow hexagons in a phase to parallelograms in β phase (see Fig. 2). This requires two Ga atoms per unit cell per O layer, as indicated by red arrows in Fig. 2, to migrate to the neighboring layers (one to the upper layer and another to the lower layer). The first step of the phase transition shown in Fig. 5 finishes half of the Ga exchange and the other half of the Ga exchange occurs at the final step, MS-G to β phase.

The diffusion length for each Ga atom in the first step is ~ 1.3 Å, and the diffusion generates three-coordinated Ga atom at the TS with a planar triangular coordination (see Fig. 5). The TS is thus highly unstable, leading to a barrier of 0.26 eV per f.u. (Fig. 2a), 60% of the overall barrier. This shows quantitatively that the Ga diffusion plays important role in the kinetics of Ga₂O₃ phase transition.



Fig. 5 The side (top panel) and top (bottom panel) views of Ga atom diffusion from α phase to MS-A state (also see Fig. 4) bypassing the transition state TS1. In the side views, the diffusional Ga atoms are highlighted by big balls with black arrows indicating the moving directions. In the top views (the atoms in the blue box of the side view), the Ga atoms above the O layer are represented by blue balls and the Ga atoms below the O layer are green balls.

In the second step, MS-A to MS-B, the Ga layers shear simultaneously with the O layers during the hcp to fcc transformation of O sublattice. One noticeable change in the step is the appearance of five- and four-coordinated Ga atoms at the interstices of O sublattice (in between 1st and 2nd layer and also in between 3st and 4th layer), as caused by the O layer shearing of 1st and 4th O layer with respect to the 2nd and 3rd O layer. Due to the formation of low coordinated Ga, the volume of crystal increases by 6.9% and the expansion occurs mainly at the direction perpendicular to the O close-packed plane. As shown in the simulated XRD, the fcc type lattice generally has its peak of close-packed plane (111)_{fcc} at 2.43 Å (peak at 16.54° in Fig. 4), which is 0.16 Å larger than that of (0001)_{hcp} plane (2.27 Å).

The Ga atom movement in the remaining steps in the phase transition resembles those in the first two steps. The rearrangement of Ga atoms destroys gradually the Ga lattice, giving poorly crystallized structure (containing GaO₅). This is evident from the simulated XRD patterns, which exhibits broad and continuous distribution of peaks at most of the intermediates, in particular from MS-C to MS-F. The displacement pattern of Ga atoms. Because of the maximum displacement length for Ga atom in the elementary step is no more than 1.5 Å, much less than the *d*-spacing of the close-packed O layers (~2.27 Å), we can conclude that the Ga displacement mainly follows the short-range reconstructive mechanism. The overall mechanism of Ga₂O₃ phase transition could be classified as pseudomartensitic solid phase transition (see Discussion section).

3.3 Biphase junctions: theory and experiment

Considering the complexity of Ga₂O₃ phase transition, it is natural for us to seek for experimental evidences to support the above theoretical results. To this aim, we have synthesized the α -Ga₂O₃/ β -Ga₂O₃ bicrystalline material using the hydrothermal experiment (see experiment detail and also previous works^{2,15,48}) and utilized the HRTEM to observe the atomic packing patterns at the biphase junctions. This bicrystalline material is prepared from GaOOH precursor, which is dehydrated first to create α -Ga₂O₃ and followed by the calcination at high temperatures (*e.g.* 600 °C). The structures of GaOOH, α -Ga₂O₃ and β -Ga₂O₃ were characterized using XRD, SEM and HRTEM techniques (see ESI[†]).

We have compared the atom pattern at the biphase junction from theory and experiment, as shown in Fig. 6. The left-hand side of Fig. 6(a-f), are images from theory including the atomic model of the most stable biphase junction (a–d), and the simulated HRTEM pictures (e and f). The HRTEM simulation was carried out using JEMS software based on the atomic structure from DFT. The right-hand side of Fig. 6(g-k) are images taken from TEM (g), selected area electron diffraction (SAED) (h), and HRTEM experiments (i–k).

Theory: the most stable interface between α -Ga₂O₃ and β -Ga₂O₃ predicted from theory is *via* the layer-by-layer packing of the O close-packed planes of two phases, *i.e.* $(001)_{\alpha}//(20\bar{1})_{\beta}$, by aligning the close-packed O rows $[120]_{\alpha}//[1\bar{3}2]_{\beta}$. We found that this interface has both the lowest strain and the best



Fig. 6 Theoretical models and experimental images of the α -Ga₂O₃/ β -Ga₂O₃ biphase junction. (a) Top-view of $(001)_{\alpha'}$; (b) top-view of $(201)_{\beta}$; (c and d) the side views for DFT optimized structures of two α -Ga₂O₃/ β -Ga₂O₃ junctions with OR $(001)_{\alpha'}/(201)_{\beta} + [120]_{\alpha'}/[132]_{\beta}$ viewing down from $[120]_{\alpha}$. The two different structures differ in β -Ga₂O₃ part, where $(111)_{\beta}$ and $(111)_{\beta}$ are crystallographically equivalent planes but have different orientation with respect to the interface; (e and f) simulated HRTEM images of α -Ga₂O₃ and β -Ga₂O₃ at $[120]_{\alpha}$ and $[132]_{\beta}$ directions, respectively; (g) TEM of a typical Ga₂O₃ rod; (h) SAED pattern taken from area B in (g) along $[120]_{\alpha}$ zone axis. (i–k) HRTEM of α -Ga₂O₃ taken from area A in (g) along $[120]_{\alpha}$ zone axis. (k) Is the enlarged image from the red box in (i), highlighting the twin structure in β -Ga₂O₃.

atomic match between two phases. As shown in Fig. 6a and b, the O-terminated $(001)_{\alpha}$ and $(20\bar{1})_{\beta}$ are remarkably similar, leading to the formation of a coherent interface. The smallest supercells with the best structural match for the two planes (dotted parallelograms in Figure) can be taken as $(001)_{\alpha}$: a = 8.72 Å; b = 8.76 Å; angle = 60.09° ; and $(20\bar{1})_{\beta}$: a = 8.79 Å, b = 8.78 Å, angle = 63.31° . This develops a low strain on the interface plane: the lattice vector mismatch below 1%; the area mismatch ~4%; and the calculated strain energy 1.922 according to the principal strain analysis from finite strain theory (the lower strain the interface has, the closer to 2 the strain energy of interface would be; see our previous publication for explanation and method^{49,50}).

Based on the interface model, two different biphase junctions can then constructed using the superlattice approach, which differ in the β -Ga₂O₃ part because (111) and (111) are two equivalent crystallographic planes but have different orientation with respect to the (201)_β interface. In our constructed biphase superlattice, 13 layers of α phase (39Ga₂O₃) joins with 13 layers of β phase (39Ga₂O₃) by sharing the O layer, forming a half-half biphase junction (see ESI†). The utilization of the long superlattice is due to the lack of periodicity in β phase at the normal direction of $(20\overline{1})_{\beta}$ ($\sim [1 \ 0 \ \overline{2.3}]$). Our DFT optimized junctions are shown in Fig. 6c and d. Using this superlattice structure, we have calculated the interface energy E_{int} , 0.54 J m⁻² according to the equation, $E_{int} = (E_{tot} - E_{\alpha} - E_{\beta})/2S$, where *S* is the interface area, and E_{α} , E_{β} , and E_{tot} are the total energies of pure α -Ga₂O₃ bulk, pure β -Ga₂O₃ bulk and the biphase superlattice, respectively.

We noticed that the structural mismatch of the current $(001)_{\alpha}//(20\bar{1})_{\beta}$ model (area mismatch ~4%) is considerably lower than the previous interface model $((110)_{\alpha}//(\bar{3}10)_{\beta})$ used by Ju *et al.*¹⁷ (area mismatch ~11%). In fact, the Ju's model can also be derived from the lowest energy pathway, as shown by the evolution of the O rows in the blue triangles in Fig. 4, indexed as $(2\bar{1}0)_{\alpha}//(3\bar{1}0)_{\beta}$ here. The OR of Ju's model is thus 19.7 degrees from the OR of the current model. Because the $(2\bar{1}0)_{\alpha}//(3\bar{1}0)_{\beta}$ interface has a larger strain and atomic misfit (see ESI†), the current $(001)_{\alpha}//(20\bar{1})_{\beta}$ interface is considered as the preferential model as biphase junctions, especially at the initial stage of phase transition (also seen the following experimental proof).

Importantly, the presence of two possible junctions shown in Fig. 6c and d suggests that the formation of $(20\bar{1})_{\beta}$ twin structures inside β -Ga₂O₃ is kinetically inevitable. The pathways leading to them are in fact energetically degenerate and thus can occur with equal probability during the β phase propagation. These different β phases are separated by $(20\bar{1})_{\beta}$ interface, forming the $(20\bar{1})_{\beta}$ twin.

Experiment: the TEM image in Fig. 6g shows the typical morphology of the synthesized α -Ga₂O₃ rod, which has its dominant growth direction along $[001]_{\alpha}$. β -Ga₂O₃ crystals start to grow from the surface of α -Ga₂O₃ rod via partial phase transition. The as-synthesized mixed phase sample remains majorly as α -Ga₂O₃ phase, as seen from the SAED pattern in Fig. 6h. The nascent β -Ga₂O₃ can be identified in HRTEM by analyzing the atomic structure on the surface of the nanorod as shown in Fig. 6i. In all HRTEM shown in Fig. 6, we keep the same zone axis as that of SAED, $[120]_{\alpha}$ (in ESI,[†] we also show the HRTEM images at the other zone axes). From this view angle, the lattice of α -Ga₂O₃ are constituted by the fringe of $(\overline{2}13)$, (006) and $(2\overline{1}3)$, as shown in figure h and j, which have the d-spacing of 4.15, 2.23, 4.15 Å, respectively. The simulated HRTEM for α -Ga₂O₃ at this zone axis shown in Fig. 6e is consistent with the experimental HRTEM in Fig. 6j.

By zooming into the interface region, we can identify the fringes with the *d*-spacing 2.62 and 4.42 Å, which have a dihedral angle 98.6°. These are characterized as $(111)_{\beta}$ and $(20\bar{1})_{\beta}$ (Fig. 6i), which are further confirmed by comparing with the simulated of β -Ga₂O₃ in Fig. 6f. The atomic structure at the interface region proves the OR predicted from theory. For example, $(006)_{\alpha}$ is found to be parallel with $(20\bar{1})_{\beta}$ (dihedral angle 1°), consistent with the $(001)_{\alpha}//(20\bar{1})_{\beta}$ relation in theory; the measured dihedral angle between $(2\bar{1}3)_{\alpha}$ and $(111)_{\beta}$ is 38.2°, which agrees nicely with the theoretical value of 39.7°.

Interestingly, the $(20\bar{1})_{\beta}$ twin are indeed common in the nascent β -Ga₂O₃ (see Fig. 6i), where $(111)_{\beta}$ is 20° away from $(11\bar{1})_{\beta}$. The dislocations at the twin interface $(20\bar{1})_{\beta}$ are also evident in HRTEM Fig. 6k, which is presumably caused by the lattice strain developed during the phase transition considering that $(001)_{\alpha}//(20\bar{1})_{\beta}$ is the biphase interface and there is ~4% area mismatch between two phases.

We also discover that a large strain is developed and present in the nascent β -Ga₂O₃ at the direction normal to the interface. While the *d*-spacing of (111) measured to be 2.62 Å, similar to (or slightly larger than) the value in the bulk value (2.55 Å), the *d*-spacing of (201) is only 2.21 Å, being much shorter than its bulk value (2.37 Å). On the other hand, this *d*-spacing of (201) in the nascent β -Ga₂O₃ is very close to that (2.23 Å) of (006) in the parent α -Ga₂O₃, where the (201) plane is evolved. This provides the direct evidence that nascent β -Ga₂O₃ is largely compressed inside the matrix of α -Ga₂O₃: the spacing between the close-packed O layers has not expanded significantly, which helps to reduce the lattice mismatch between two phases. In this case, the strain energy due to the compressed β phase is compromised by the interface energy at the phase junction.

4. Discussions

4.1 Pseudomartensitic phase transition mechanism

The reaction pathway of $Ga_2O_3 \alpha - \beta$ solid phase transition identified above provides a detailed example of pseudomartensitic phase transition pathway. We are therefore at the position to discuss some general features of pseudomartensitic phase transition based on the understandings achieved in this work. In Fig. 7, we draw the schematic diagram of pseudomartensitic phase transition in comparison with three typical diffusionless solid phase transition mechanisms, including the martensitic mechanism, reconstructive mechanism and dilation mechanism. The martensitic mechanism features the shearing of atom layers, involving lattice distortions but no significant volume change.^{51,52} The strain-invariant plane (black line in Fig. 7) and strain-invariant line (also known as the undistorted line) can be identified as the macroscopic evidences of martensitic transition. Different from the martensitic mechanism, the reconstructive transition involves mainly the local arrangement of atoms with little change on the crystal lattice.⁵² The dilation transition, by its name, must involve a significant expansion/compression in the phase transition and in general no undistorted line can be identified. It is unlikely to form coherent interface in the dilation transition due to the large strain energy of the new phase inside the parent phase.

From the structural point of view, pseudomartensitic phase transition has a great similarity with martensitic phase transition, but may also mix with the features of the other two types of mechanisms. In $Ga_2O_3 \alpha - \beta$ solid phase transition, we find



Fig. 7 Schematic illustration of four diffusionless solid phase transition mechanisms, including martensitic, dilation, reconstructive and pseudo-martensitic phase transition mechanism.

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that the O sublattice movement is fundamental to the process, which dictates the crystallographic OR and leads to the formation of coherent interface between two phases. Not surprisingly, the strain-invariant plane and the strain-invariant line are present, similar to martensitic phase transition. On the other hand, pseudomartensitic transition is naturally a multi-step and multitype reaction, not only having the shearing movement, but also including the reconstructive movement of local atoms and, possibly, the significant lattice expansion (see Fig. 7). All these different movements are assembled in one reaction but could occur at different stages depending on reaction conditions. From the pathway of Ga₂O₃ transition, we see that the Ga local diffusion can occur independently without involving the O laver shear. Furthermore, the observed atomic structure of nascent β phase from experiment suggests the late occurrence of β phase lattice expansion. This is in line with the multistep, multitype nature of pseudomartensitic transition where a coherent interface is present to facilitate the new phase growth. The lattice dilation would occur only when the domain of β Ga₂O₃ reaches to a certain (large) size until the energy cost of interface mismatching can be overcome by the strain release of β Ga₂O₃ microcrystals.

From the thermodynamics and kinetics point of view, pseudomartensitic phase transition is quite different from other types of phase transitions. Because of the multi-type nature of the reaction, the phase transition can be initiated rapidly, but the completion of the phase transition is considerably slow. The former is the consequence of martensitic phase transition, which usually has a low barrier due to the low strain, coherent interface for phase propagation. The latter is due to the high barrier of atom restructuring and local diffusion, which requires a large heat input to break/form local bonds while keeping the structure of the other parts of crystal.

4.2 General rules for predicting product crystallinity

The nature of Ga₂O₃ phase transition as pseudomartensitic phase transition can explain the apparently contradictory observations on its reaction kinetics and the product crystallinity at different pressure and temperature conditions. The high pressure can induce rapidly the β to α transition even at room temperatures, which however leads to the apparent amorphization of the crystal, as implied from XRD and Raman spectra.¹² We expect that this is largely due to the fact that the Ga atom local reordering in Ga₂O₃ has a much higher barrier than the pressure-induced shearing of atom layers and thus cannot occur rapidly at low temperatures. From the pathway shown in Fig. 4, we found that the intermediates after Ga local diffusion have broad XRD pattern and are indeed "amorphous-like" despite the presence of structurally ordered O sublattice. To speed up the Ga reconstructive reactions, a high temperature is required to enhance the phonon vibration of solids. Therefore, it is not surprising that the high-temperature sintering of α -Ga₂O₃ do produce well-crystallized β-Ga₂O₃.

With the advent of SSW pathway sampling, we anticipate that the simulation of even complex solid phase transitions at the atomic level is now within the reach of modern computational power. This is because the atom diffusion in solid, if occurring, has to be site-by-site due to the packing of atoms in lattice and thus a complex solid phase transition can always be separated into multiple elementary steps, similar to that in molecular reactions. The decoupling of different types of atomic displacements that belong to different vibrational modes enables the description of solid phase transition in relatively small unit cells, which are accessible by SSW-based global pathway screening.

The reaction pathway with all the elementary steps determined provides the key information on kinetics, which could be utilized for predicting the product crystallinity, as summarized into three general rules in the following:

(i) If the martensitic shear is the rate-determining movement in solid phase transition, it could form coherent interfaces and yield well-crystallized products. Since the atomic layer shearing generally has a low barrier, such phase transitions could occur at relatively low temperatures.

(ii) If the reconstructive or dilation movement is the ratedetermining step, the crystallization of the final product could be slow and often requires high temperatures. For this reason, such reactions have the tendency to produce poorly crystalized (with different microstructures) and even amorphous phases.

(iii) Pseudomartensitic transition has features of (i) and (ii) above, and thus can lead to both amorphous-like and crystalline products depending on reaction temperature. The presence of a structurally ordered sublattice during the phase transition is a key characteristic.

5. Conclusion

 $Ga_2O_3 \alpha - \beta$ phase transition represents a common class of solid phase transitions, where atoms (cations) vary their coordination environment to induce a significant volume change. Using the state-of-the-art theoretical and experimental techniques, including SSW pathway sampling and HRTEM, this work determines the atomistic mechanism of $Ga_2O_3 \alpha - \beta$ phase transition, which provides a first example to look into the atomic level detail of pseudomartensitic solid phase transition. The atom displacement patterns learnt from the pathway helps to clarify long-standing puzzles on Ga₂O₃ phase transition and deepen our understandings on complex solid phase transition reactions in general. The new knowledge on the kinetics of pseudomartensitic solid phase transition is an important and essential complement to the theory of diffusionless solid phase transition, and is also beneficial for the rational design of material with desired crystallinity and properties. Our major results are outlined below.

(i) $Ga_2O_3 \alpha -\beta$ phase transition involves repeated hcp-fcc transformation of O sublattice by the shearing of the close-packed O layers, which obeys martensitic mechanism. This leads to the formation of low-strain, atomically matched interface between two phases and the presence of a simple crystallographic OR: $(001)_{\alpha}//(20\bar{1})_{\beta}$ and $[120]_{\alpha}//[1\bar{3}2]_{\beta}$.

(ii) The phase transition has a long periodicity featuring non-collective Ga reordering: a large 60-atom unit cell is required

to capture the Ga atom displacement in the phase transition. We identify the lowest energy pathway that has 7 intermediate phases and the calculated overall barrier is 0.43 eV per f.u. The Ga migration through the close-packed O layers is the rate-determining step.

(iii) Bicrystalline Ga_2O_3 samples are synthesized and analyzed using HRTEM. The experimental observation at the biphase junction confirms the theoretical prediction on OR and the presence of $(20\bar{1})_\beta$ twin.

(iv) Ga₂O₃ α - β phase transition is classified as pseudomartensitic mechanism, which can lead to both amorphous-like and crystalline products depending on temperature. We define pseudomartensitic solid phase transition as a multi-step, multi-type diffusionless solid phase transition, where the presence of a structurally ordered sublattice during phase transition is a key characteristic.

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