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Electronic Supplementary Information : Designing porous-crystalline structure of β-Ga_2O_3: a potential approach to tune its opto-electronic properties

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1 Validation of present model

We have pointed out (in the introduction section of the main-text) that the regular hexagonally aligned and parallel channel can be experimentally synthesized [F. Li, L. Zhang, R.M. Metzger, Chem. Mater, 10, 2470, 1998]. We also expect that even for disordered systems, the main feature of band gap reduction can retain. While it is difficult to comprehensively study the disorder effect theoretically, the pore-pore interaction can be revealed in some degree by comparing the properties of small vs. large size channel. The similarity of their results, and the localization of the band edge states at the channel surface rule out the possibility of strong interaction between neighboring channels. In fact, the band gap reduction occurs due to the raising of VBM energy and lowering the CBM energy, which becomes relatively localized at the surface O and Ga sites, respectively, we do not expect it to change significantly with the pore-size. To test this hypothesis, we have calculated another system (see Figure 4) which doubles the size of the pore and consists of total 600 atoms (with 2x4x4 supercell). We see similar band gap reduction and similar band edge states (see Figure 5). Calculated with PBE, the band gap is 0.65 eV compared to the 0.70 eV band gap for the smaller channel size. More importantly, the VBM and CBM states look similar for the large and small sized channel cases (see Figure 5). Unfortunately, for this larger system, it is too expensive to use the HSE, but the similarity of the PBE results strongly indicate that the discovered phenomena remains in large pore size cases as well. Hence, we have carried out the final set of calculations with a structural model of 1x4x2 supercell (containing 150 atom) with reasonable computational cost and accuracy, although the size of the channel is little smaller compared to the experiment.

2 Computational details

Calculation of optical properties with atom centred basis set as implemented in SIESTA is computationally affordable for hundreds of atoms and it maintains the accuracy as well. This allows us to deal with porous supercell structure containing 150-200 atoms at reasonable computational cost. In addition, we have compared the results of our electronic structure calculations using the Norm-Conserving pseudo potential with atom-centred basis set as implemented in SIESTA and the PAW pseudo potential in Quantum Espresso. For both the methods, the relative stability of the different channel configurations and pure Ga_2O_3 are in close match with similar trend. We have also compared the PBE band gap from two calculation set-ups, which also matches with each other. These results prove the consistency and robustness of the result irrespective of the different basis-sets for PBE-based calculations on Ga_2O_3 system. So, we have carried out the calculations on optical properties using the smarter way as implemented in SIESTA to reduce the computational cost.

3 Results & discussion on larger pore model

To understand the effect of the size of the pore in the porous-crystalline Ga_2O_3, we have considered a model with larger pore-diameter, as shown in Figure 4. Even after consideration of larger pore-sized Ga_2O_3 (as shown in Figure 4), we find the band gap to be 0.65 eV which is comparable to the gap of 0.70 eV as found in case of almost half-sized porous channel. Hence, we emphasise that the optoelectronic property is attributed to the states which are localised predominantly at vacancy channel. The electron and hole states for bigger channel also reside at spatially distinct locations (see Figure 5), as found for smaller channel as well (see the right panel of Figure 7 in the main-article). Thus, the basic features, i.e., the reduced band-gap and spatial separa-

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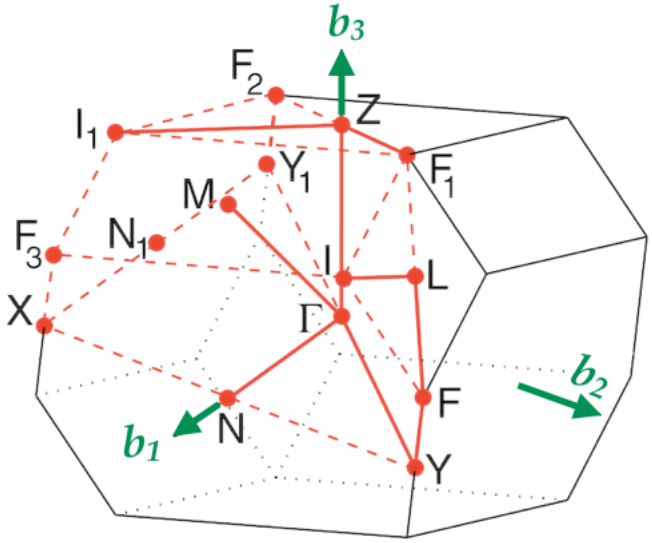

Fig. 1 The Brillouin zone of the monoclinic $\beta - Ga_2O_3$. Both types of high-symmetry points, i.e., trivial and nontrivial points are indicated.

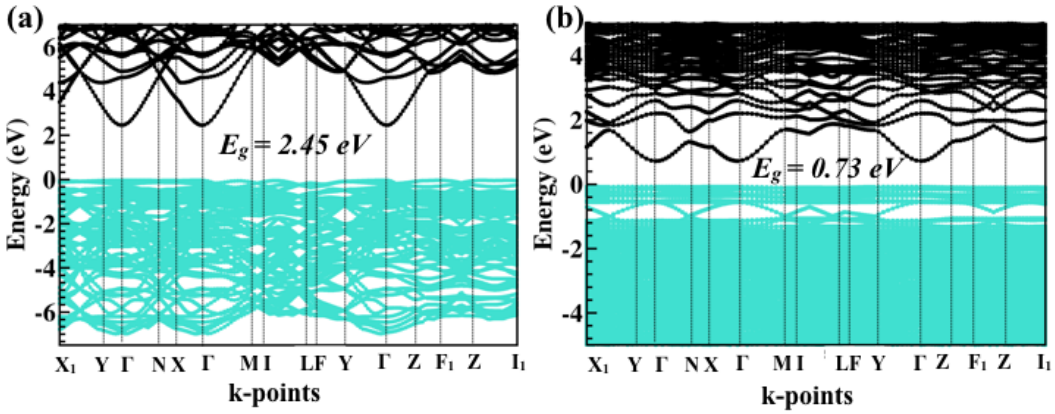

Fig. 2 PBE band structure of (a) pure β-Ga_2O_3 and (b) V-2 are shown along the defined path in the Brillouin zone.

tion of electron-hole states for porous-crystalline Ga_2O_3 is robust and does not change significantly with the size of the pore.

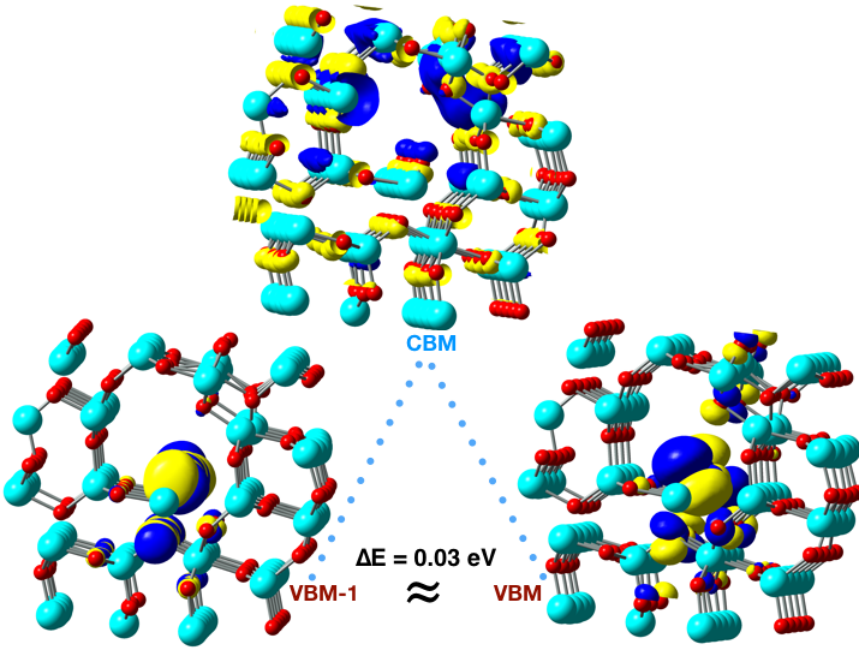

Fig. 3 Nature of VBM-1, VBM, and CBM at the gap state (Γ-point). wavefunction plots are in real space with isovalue 0.02.

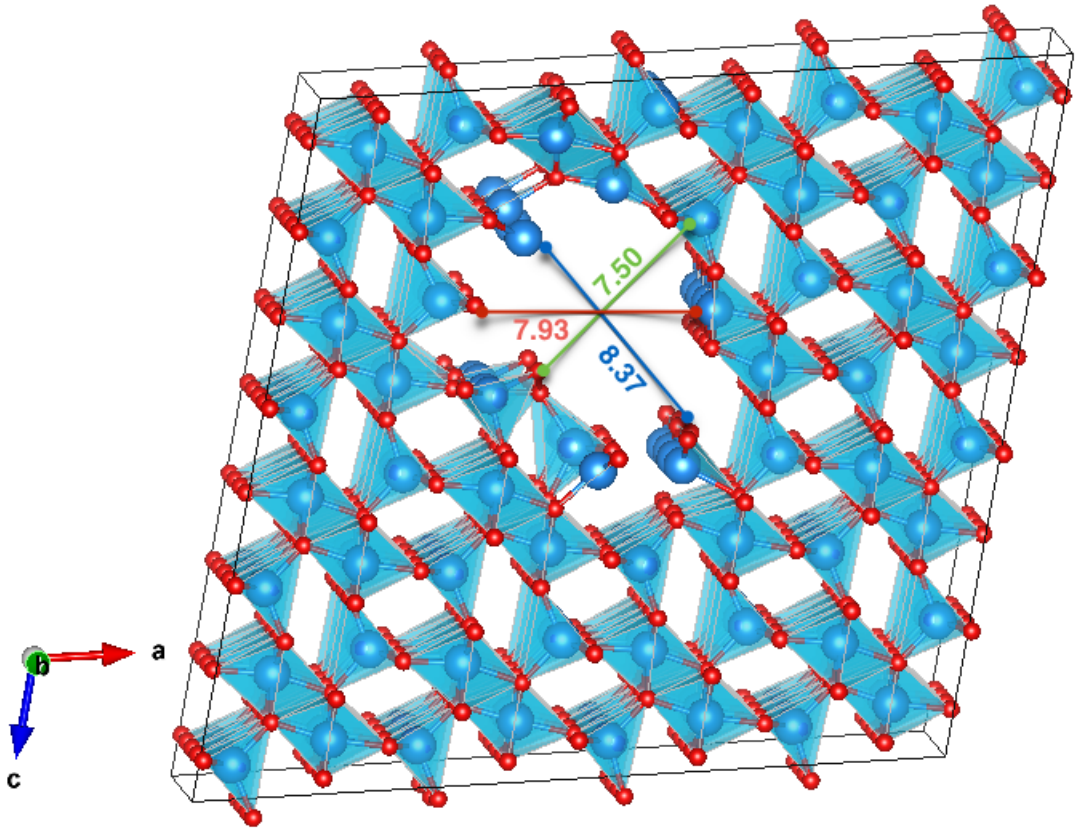

Fig. 4 Optimised structure with 1D vacancy channels along y is shown, pore diameters are indicated in unit. 2x4x4 supercell of monoclinic β-Ga_2O_3 (600 atoms) have been used and the vacancy channel has larger pore diameter than the same discussed in Figure 2 and 3 in the main-text. Blue: Ga; Red: O.

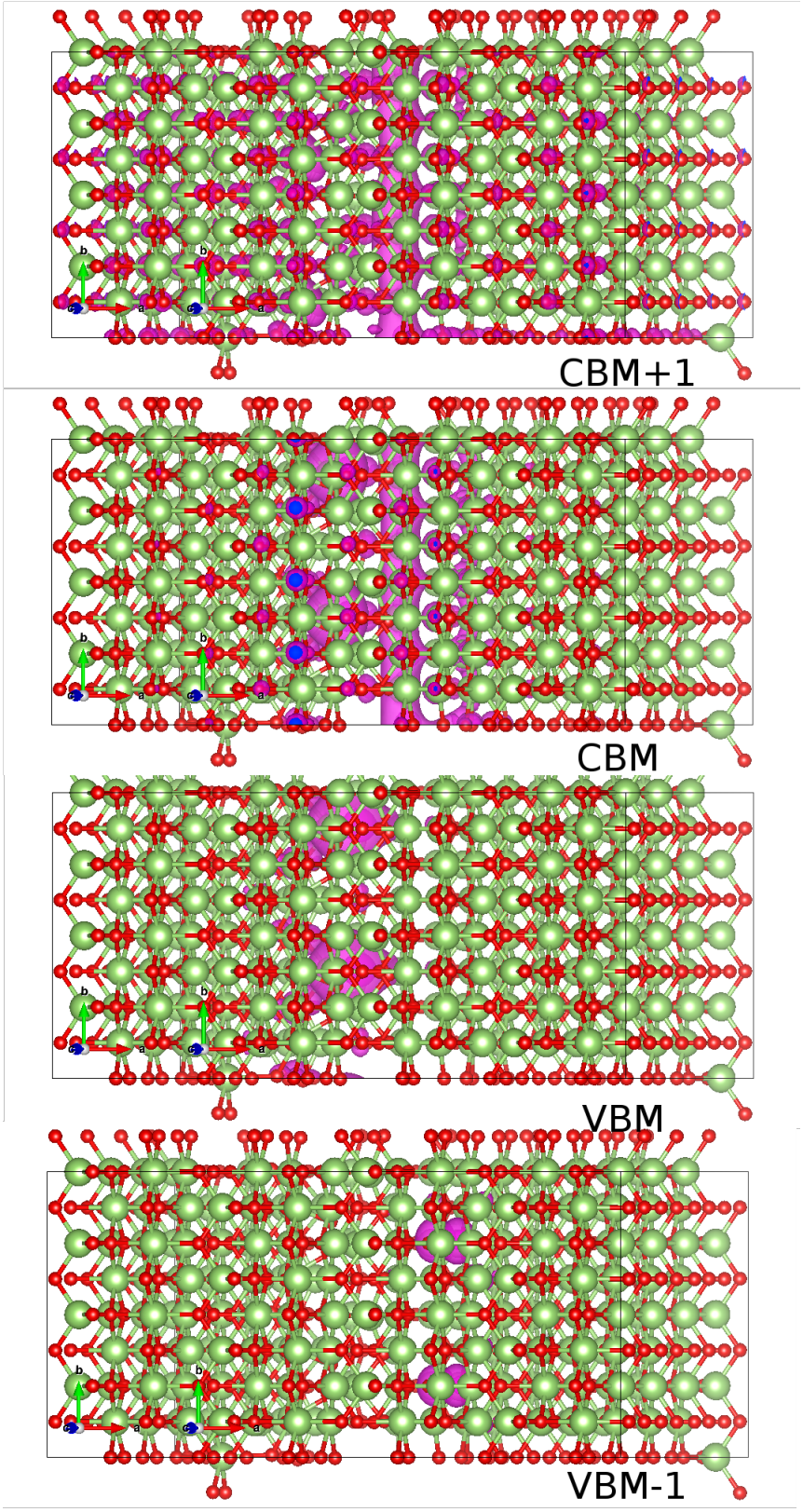

Fig. 5 Nature of VBM-1, VBM, CBM, CBM+1 at the gap state (Γ-point) for the porous structure, as described in previous figure (Figure 4). Wavefunction plots are in real space with isovalue 0.02. Green: Ga; Red: O.