

PAPER

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Optical properties of ideal γ - Al_2O_3 and with oxygen point defects: an *ab initio* study

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The optical properties of pure γ - Al_2O_3 and in the presence of oxygen point defects are investigated by the density functional theory approach using the PBE-GGA and TB-mBJ-GGA schemes. The optical properties of the modeled imperfect crystal show closer agreement with the experimental results than the ideal crystal. The defects produce extra sharp bands and sub-bands, in the bandgap region. The TB-mBJ scheme provides better descriptions of the bandgaps and positions of the sub-bands compared to the experiments than the PBE-GGA scheme. The imaginary part of the dielectric function reveals that the sub-bands produced by the oxygen point defects act as trapping centers. The real part of the dielectric function and the index of refraction are also strongly affected by these defects and increase at 0 eV, decrease at 5 eV and remain constant at 80 eV with the defects. The intensities of the optical spectra are calculated by PBE-GGA to be higher than those of TB-mBJ. The higher intensities are mainly ascribed to the matrix elements of the linear momentum operator.

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1 Introduction

Alumina (Al_2O_3) is one of the most important ceramic materials with exceptional properties such as great hardness, chemical inertness, and a high melting temperature.^{1,2} It has many industrial applications such as catalysis, coatings, microelectronics, optical materials, and advanced material technology.^{3,4} Besides the stable α - Al_2O_3 phase, alumina can also exist in a number of metastable polymorphs such as β (hexagonal), γ (cubic spinel), η (cubic spinel), θ (monoclinic), κ (orthorhombic), and δ (tetragonal).^{3,5} Most of the Al_2O_3 polymorphs exhibit good thermal and chemical stability. They are used in a variety of applications depending on their specific surface properties. Among them, sapphire (α - Al_2O_3) is the most stable and hard phase, and is used for ultra-hard coatings. Sapphire is widely used in optical applications as a substrate for thin film optical devices, like LEDs, optical data storage devices, *etc.*⁶ However, α - Al_2O_3 can only be formed at temperatures higher than 1000 °C; at lower temperatures only the metastable Al_2O_3 polymorph phases can be synthesized.⁷ Among the different Al_2O_3 phases, γ - Al_2O_3 has more significant importance in nanotechnology. This material can be formed at low temperatures, greater than 350 °C (ref. 8) which make it suitable for

microelectronic processing.⁹ Therefore, theoretical and experimental investigations of the optical properties of γ - Al_2O_3 or its analogous structures may be very interesting. Semiempirical^{10,11} and *ab initio*^{12,13} schemes based on density-functional theory (DFT)^{14,15} have been employed to determine the electronic band structure of γ -alumina. Concerning the optical response and related dielectric functions, the first-principles calculations^{5,16} are based on both independent-particle (IP)¹⁷ and Bethe-Salpeter equation (BSE)¹⁸ approximation levels. The latter scheme is more accurate, incorporating many-body effects in the electron response, however the computational cost of BSE calculations is much more expensive than IP calculations.^{19,20} In order to overcome the time consuming nature of these calculations, a restricted version of the excitation spectrum was reported for alumina.¹⁹ In anticipation of further study, in this work we restricted the accuracy to the IP calculations. In practice an experimentally synthesized γ - Al_2O_3 usually, depending on the preparation and treatment, contains a number of different point defects including oxygen and/or aluminum vacancies.^{21–24} A doubly positively charged oxygen vacancy is not electronically stable. This defect can create either a singly ionized or a neutral oxygen vacancy *via* trapping one or two electrons, respectively. The latter defects are generally called F-centers. The study of point defects is important in solids, because they can substantially influence the mechanical, electronic, thermal, and optical properties of the materials.^{25–29} It is well-known that F-centers have a key contribution to the optical properties of the synthesized Al_2O_3 crystal.^{30–32} It is, therefore, very important to understand the structures and chemistry of point defects in Al_2O_3 . Hence, we aim to investigate the effects of the neutral

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oxygen vacancies (F-centers) on the optical properties of the compound. We analyze our calculated optical results in the absence and presence of these defects. Our calculated optical results in the absence of the intrinsic point defects within PBE-GGA are in agreement with the previous FP-LMTO results,⁵ while our optical results in the presence of the defects show good agreement with the available experimental data.³³ This study verifies that the consideration of the oxygen defects could cause the results to be in better agreement with the available experimental data compared to the ideal γ -Al₂O₃ compound. We observe that the intensities of the optical spectra predicted by TB-mBJ are lower than those predicted by PBE-GGA. This observation is in agreement with the previous results of the other cases.^{34,35} We show that the lower intensities mainly originate from the fact that the matrix elements of the linear momentum operator, as appeared in the dielectric functions, are calculated by TB-mBJ to be not exactly the same as PBE-GGA.

2 Computational details

Based on the previous X-ray studies, the structure of γ -Al₂O₃ is described as a defective spinel, denoted as $\square_{\frac{2}{3}}\text{Al}_{\frac{1}{3}}\text{O}_{32}$, where

the “ $\square$ ” symbol stands for the Al vacancy to satisfy the stoichiometry of the formula.³⁶ Pinto and coworkers³⁷ changed the basis vectors of this structure in order to produce a hexagonal structure, as reviewed in detail in our previous work.³⁸ This hexagonal crystal structure was also used in this study (see Fig. 1(a)). In principle, the ideal structure of γ -Al₂O₃ can be constructed. In practice, γ -Al₂O₃ contains Al and/or O intrinsic point defects.^{23,24,39} These point defects can change the optical properties of the system. Thus, it may be crucial to create the crystal structure in the presence of these point defects. In order to simulate the intrinsic point defects, we introduce oxygen vacancies by removing O atoms from the ideal structure. There are two different types of oxygen atoms in the ideal structure. The type of O depends on its point group symmetry, which can be distinguished by its coordination number. The coordination number can be 3 or 4 for O. After removing an O atom from the ideal structure, an O vacancy is formed in the position of the removed O atom. The O vacancy is denoted as V_{On}, where n can be 3 or 4 to indicate the coordination number of the removed O atom. The two types of O vacancies V_{O3} and V_{O4} are shown in Fig. 1(b) and (c), respectively. V_{O3} and V_{O4} are our used intrinsic point defects in the present work. All our calculations were carried out by the reliable WIEN2k code⁴⁰ to solve self-consistently the scalar-relativistic Kohn–Sham equations based on density functional theory using the augmented plane waves plus local orbitals (APW + lo) method. For the exchange–correlation term, the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) was used.⁴¹ The bandgap calculations were improved by the TB-mBJ method.^{42,43} The bandgap was further improved by performing non-regular TB-mBJ calculations using the optimized c -factor (c_{opt}). The c_{opt} was found to be 1.8 for the ideal γ -Al₂O₃.³⁸ In this work, we perform GGA and non-regular TB-mBJ with $c_{\text{opt}} = 1.8$ calculations for the defective spinel structures in the presence of the

intrinsic point defects V_{O3} and V_{O4}. After introducing each vacancy, the ions were allowed to relax until the forces are less than 1 mRy Bohr^{−1}. In the FP-LAPW method, the unit cell was divided into nonoverlapping spheres centered at atomic sites (muffin-tin spheres) of radius R_{MT} and an interstitial region. The muffin-tin radii were taken to be 1.51 (Bohr) for both Al and O. The plane waves expansion of the wave function in the interstitial region was truncated at $R_{\text{MT}}K_{\text{MAX}} = 7$, where K_{MAX} is the plane-waves cut-off and R_{MT} is the smallest of all the atomic sphere radii. Self-consistency was obtained by using 96 k -points in the first irreducible Brillouin zone (1BZ). The cut-off energy, which defines the separation of the valence and core states, was chosen to be −8 Ry. The number of bands included in the calculations is 322 for the ideal case and 316 for the defective cases. The accuracy of predicting the peaks of the imaginary part of the dielectric function depends on the number of k -points; denser mesh gives better results.⁴⁴ Therefore, for the optical property calculations, the number of k -points was once more optimized and ultimately increased from $8 \times 8 \times 3$ with 96 k -points in the first irreducible Brillouin zone (1BZ) to a denser mesh of $16 \times 16 \times 5$ with 640 k -points in the 1BZ.

3 Electronic structure

3.1 Band structures and subbands generated by intrinsic oxygen defects

The calculated band structures for the ideal spinel structure using TB-mBJ and non-regular TB-mBJ are compared with that of the non-ideal structure using non-regular TB-mBJ in Fig. 2. The result for the ideal structure within regular TB-mBJ, as plotted in Fig. 2(a), shows a direct bandgap of 6.22 eV at the Γ -point. The band gap was improved to 8.02 eV utilizing non-regular TB-mBJ,³⁸ as shown in Fig. 2(b), which is in better agreement with the experimental bandgap⁴⁵ of 8.7 eV. Although we have considerably improved the bandgap by means of the non-regular TB-mBJ method, one would keep in mind that underestimation of the gap width is also to be expected from the unknown exact potential of Kohn–Sham density-functional theory, because of derivative discontinuities of the exchange–correlation energy.^{46,47} This means that the bandgap even with

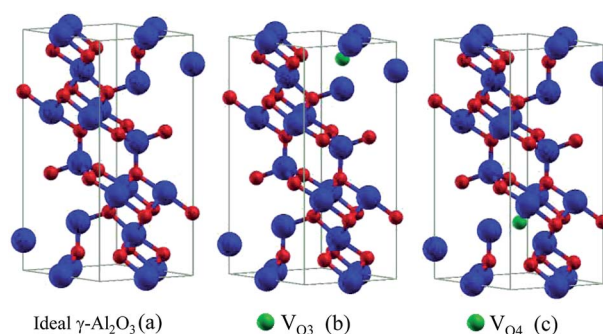


Fig. 1 The ideal (a) and defective hexagonal spinel structures in the presence of the intrinsic point defects V_{O3} (b) and V_{O4} (c). V stands for vacancy and numbers are used to show the coordination numbers of the removed O atom.

the exact functional severely underestimates the fundamental gap.⁴⁸ The bands of the ideal case, discussed in ref. 38, were reproduced as a criterion to realize the effects of intrinsic point defects. The O vacancies are experimentally predominant in $\gamma\text{-Al}_2\text{O}_3$.^{21,24} Thus, the natural defect subbands mainly originate from the O vacancies compared to the Al vacancies. This indicates that it is more reasonable to calculate the induced subbands in the presence of O vacancies than that of Al vacancies. Hence, the band structure of the system in the presence of the $\text{V}_{\text{O}4}$ intrinsic point defect was calculated within non-regular TB-mBJ with $c_{\text{opt}} = 1.8$, see Fig. 2(c). The band structure in the presence of the $\text{V}_{\text{O}4}$ vacancy shows that extra bands, *i.e.*, subbands, are produced by the $\text{V}_{\text{O}4}$ defect. The formation of the oxygen vacancy generated donor-like sublevels below the conduction band minimum.

3.2 Partial DOSs and transitions permitted by selection rules

A strong relation exists between the partial DOSs (PDOSs) and the imaginary part of the complex dielectric function, $\mathcal{I}[\varepsilon(\omega)]$. Partial DOSs are presented here for $\gamma\text{-Al}_2\text{O}_3$ in Fig. 3(a–e), for $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$ in Fig. 3(f–j), and for $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$ in Fig. 3(k–o). The PDOSs were calculated within TB-mBJ. TB-mBJ can give a satisfactory bandgap, which can be more appropriate for predicting the transition energies. In this case, for the semiconductor compounds one does not necessarily need to shift the $\mathcal{I}[\varepsilon(\omega)]$ spectrum to force it to be comparable with experiments. The sizable discrepancy between the theoretical bandgap within LDA or GGA and the experimental bandgap can be substantially reduced, if one uses TB-mBJ instead of LDA or GGA. The states for which the interband transitions between them can occur are marked by A_i ($i = 1$ to 9) for the ideal $\gamma\text{-Al}_2\text{O}_3$ in Fig. 3(a–e), and by B_i and C_i ($i = 1$ to 10) for $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$ and $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$ in Fig. 3(f–j) and (k–o), respectively. We will

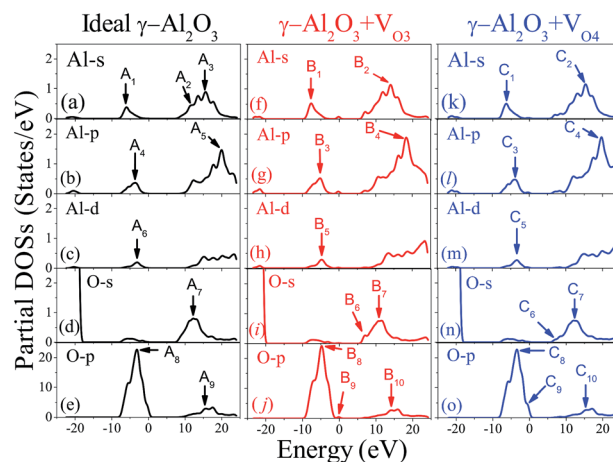


Fig. 3 The calculated partial DOSs within TB-mBJ for the ((a) to (e)) ideal structure, and the defective spinel structure in the presence of the intrinsic point defects ((f) to (j)) $\text{V}_{\text{O}3}$, and ((k) to (o)) $\text{V}_{\text{O}4}$. The Fermi level in eV is set to zero.

analyze both PDOSs and $\mathcal{I}[\varepsilon(\omega)]$ functions to determine the direct interband transitions which can occur in practice. Here, in this section, we only consider PDOSs. The PDOSs show that a very short peak marked by B_9 at -0.01 eV in Fig. 3(j) is created by the intrinsic point defect $\text{V}_{\text{O}3}$ in the valence region of the $\text{O}|p\rangle$ DOS for $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$ compared to the $\text{O}|p\rangle$ DOS of the ideal case shown in Fig. 3(e). A shoulder which is marked by B_6 at 6.78 eV in Fig. 3(i) is also created by the $\text{V}_{\text{O}3}$ defect in the conduction region of the $\text{O}|s\rangle$ DOS for $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$ when compared to that of the ideal case shown in Fig. 3(d). The latter created B_6 peak is indeed the subbands produced by $\text{V}_{\text{O}3}$ in the bandgap region of the ideal case. The former created B_9 peak plays a key role in the transition to the latter created B_6 subbands, as will be discussed in

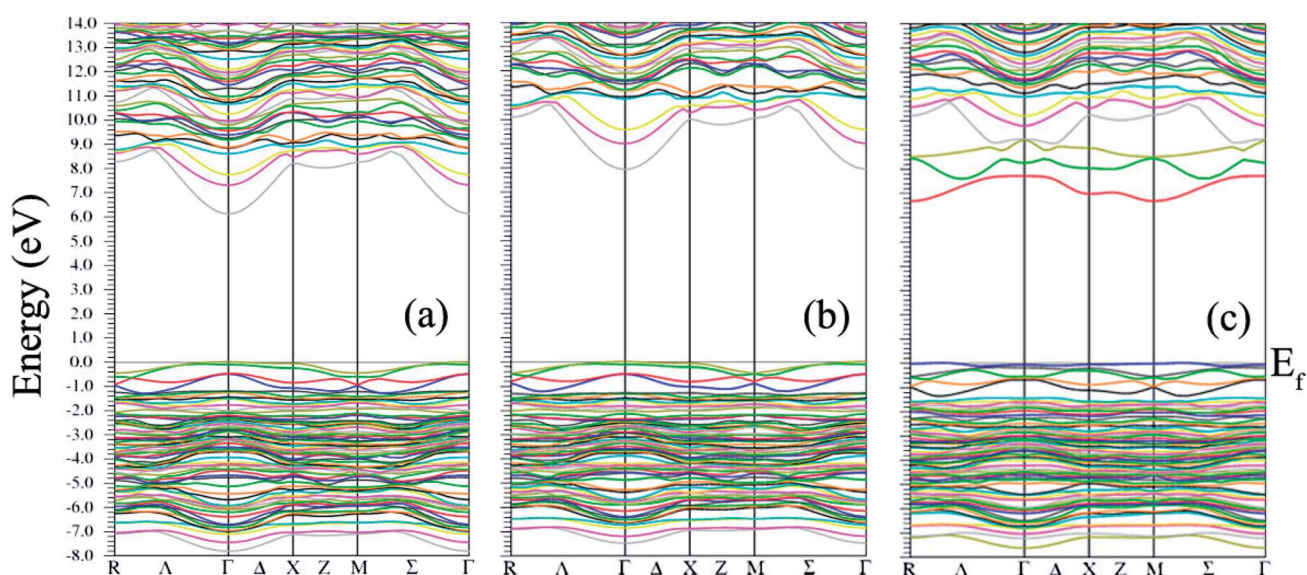


Fig. 2 The calculated band structures for the (a) ideal structure within regular TB-mBJ, and (b) ideal structure within non-regular TB-mBJ with $c_{\text{opt}} = 1.8$, as well as (c) the defective spinel structure in the presence of the $\text{V}_{\text{O}4}$ intrinsic point defects within non-regular TB-mBJ with $c_{\text{opt}} = 1.8$. The Fermi level in eV is set to zero.

Table 1 The permissible interband transitions, both absorptions ($\rightarrow$) and emissions ($\leftarrow$), based on the selection rules, $\Delta l = 0, \pm 1$ (no $0 \rightarrow 0$ transition), derived from the Wigner–Eckart theorem due to non-zero Clebsch–Gordan coefficients for a spherical tensor of rank 1

Transition	Δl	Transition	Δl	Transition	Δl
$O s\rangle \rightleftharpoons O p\rangle$	± 1	$O s\rangle \rightleftharpoons Al p\rangle$	± 1	$O p\rangle \rightleftharpoons Al s\rangle$	± 1
$O p\rangle \rightleftharpoons Al d\rangle$	± 1	$Al s\rangle \rightleftharpoons Al p\rangle$	± 1	$Al s\rangle \rightleftharpoons O p\rangle$	± 1
$Al p\rangle \rightleftharpoons Al s\rangle$	± 1	$Al p\rangle \rightleftharpoons Al d\rangle$	± 1	$Al d\rangle \rightleftharpoons O p\rangle$	± 1
$Al d\rangle \rightleftharpoons Al p\rangle$	± 1				

Table 2 The labelled peaks of the $\mathcal{J}[\varepsilon(E)]$ spectra (ε_2) and their associated energies (E_{ε_2}), labelled valence peaks of the PDOSs (DOS_v) and their associated energies (E_v), labeled conduction peaks of the PDOSs (DOS_c) and their associated energies (E_c), energy differences between the conduction and valence peaks ($|\Delta E_{v \rightarrow c}| = E_c - E_v$) and their associated selection rules (Δl)

ε_2	E_{ε_2}	DOS_v	E_v	DOS_c	E_c	$ \Delta E_{v \rightarrow c} $	Transition	Δl
Ideal γ-Al_2O_3								
a ₁	14.70	A ₈	−3.14	A ₂	11.55	14.69	$O p\rangle \rightleftharpoons Al s\rangle$	± 1
a ₂	15.93	A ₄	−3.58	A ₇	12.30	15.88	$Al p\rangle \rightleftharpoons O s\rangle$	± 1
a ₃	18.62	A ₈	−3.14	A ₃	15.46	18.60	$O p\rangle \rightleftharpoons Al s\rangle$	± 1
a ₄	21.73	A ₁	−6.03	A ₉	15.70	21.73	$Al s\rangle \rightleftharpoons O p\rangle$	± 1
a ₅	23.06	A ₆	−3.07	A ₅	19.95	23.02	$Al d\rangle \rightleftharpoons Al p\rangle$	± 1
γ-Al_2O_3 + V_{O3}								
b ₁	6.81	B ₉	−0.01	B ₆	6.78	6.79	$O p\rangle \rightleftharpoons O s\rangle$	± 1
b ₂	16.23	B ₃	−5.16	B ₇	11.02	16.18	$Al p\rangle \rightleftharpoons O s\rangle$	± 1
b ₃	18.81	B ₈	−4.79	B ₂	13.98	18.77	$O p\rangle \rightleftharpoons Al s\rangle$	± 1
b ₄	21.82	B ₁	−7.64	B ₁₀	14.18	21.82	$Al s\rangle \rightleftharpoons O p\rangle$	± 1
b ₅	23.14	B ₅	−4.72	B ₄	18.37	23.09	$Al d\rangle \rightleftharpoons Al p\rangle$	± 1
γ-Al_2O_3 + V_{O4}								
c ₁	7.11	C ₉	−0.18	C ₆	6.90	7.08	$O p\rangle \rightleftharpoons O s\rangle$	± 1
c ₂	16.34	C ₃	−3.93	C ₇	12.39	16.32	$Al p\rangle \rightleftharpoons O s\rangle$	± 1
c ₃	18.80	C ₈	−3.42	C ₂	15.32	18.74	$O p\rangle \rightleftharpoons Al s\rangle$	± 1
c ₄	21.96	C ₁	−6.31	C ₁₀	15.65	21.96	$Al s\rangle \rightleftharpoons O p\rangle$	± 1
c ₅	23.14	C ₅	−3.35	C ₄	19.70	23.05	$Al d\rangle \rightleftharpoons Al p\rangle$	± 1

Section 4.2. Similarly, two shoulders are created by the V_{O4} defects in the valence and conduction regions. These shoulders are labeled by C_9 at -0.18 eV in Fig. 3(o) and C_6 at 6.9 eV in Fig. 3(n). The C_6 shoulder is the subbands produced by V_{O4} in the bandgap region of the ideal case. The C_9 and C_6 shoulders or peaks will make transition from the valence state to the subbands possible, as will be discussed in Section 4.2. According to the selection rules, $\Delta l = 0, \pm 1$ regardless of the forbidden $0 \rightarrow 0$ transition, the permissible interband transitions which can take place in principle for γ - Al_2O_3 are listed in Table 1. We investigate practically the permissible interband transitions by calculating the imaginary part of the dielectric function in Section 4.2. Eventually, among the allowed transitions listed in Table 1, we keep those transitions that were also consistent with $\mathcal{J}[\varepsilon(\omega)]$ and omit the inconsistent ones in Section 4.2. It is important to note that the Kohn–Sham wave function obtained by the DFT calculations could present hybridization and thereby the compounds could lose their atomic characters. Indeed, in contrast to the isolated atoms the calculated DOSs of the

compounds were broadened due to the existing interactions in their crystalline environment and as a result they were no longer sharp and delta function-like. Therefore, matching the projected DOS and absorption peaks to find the possible transitions sometime needs careful practical elaborations, as performed in Table 2.

4 Optical properties

4.1 Theoretical background and disclaimer

The theoretical background of the linear optical properties of solids in the framework of the FP-LAPW method as embedded in the WIEN2k code were discussed in detail by Ambrosch-Draxl and Sofo.⁴⁴ Here, we provide a brief review by emphasizing on the approximations made and thereby the limitations caused in the formulas used for our optical properties calculations. This validates the accuracy of the presented optical properties results in the subsequent sections for the solid systems in question. The response potential, $V_G(\mathbf{q}, \omega)$, of a solid to the incident transverse time-dependent electromagnetic waves was investigated by the $V_G(\mathbf{q}, \omega) = \sum_{\mathbf{G}'} \varepsilon_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega) V_{\mathbf{G}'}^{\text{ext}}(\mathbf{q}, \omega)$ relation in the

limit of $\mathbf{q} \rightarrow 0$ for $\mathbf{G}'$ and $\mathbf{G} = 0$. In this relation, $V_{\mathbf{G}'}^{\text{ext}}(\mathbf{q}, \omega)$ which is produced by the incident light is the external perturbation potential, $\mathbf{G}$ and $\mathbf{G}'$ are reciprocal lattice vectors, $\varepsilon_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega)$ is the inverse of the dielectric tensor, and $\mathbf{q}$ and ω are the wave-vector and angular frequency of the incident light, respectively. The limit of $\mathbf{q} \rightarrow 0$ indicates that q is much smaller than the magnitude of any typical wavevectors of electrons in the solids. The problem of finding the responses of the solids to the incident electromagnetic fields was reduced to solve $V_0(0, \omega) = \varepsilon_{0,0}^{-1}(0, \omega) V_0^{\text{ext}}(0, \omega)$ and thereby to find $\lim_{\mathbf{q} \rightarrow 0} 1/\varepsilon^{-1}(\mathbf{q}, \omega) \equiv \varepsilon(\omega)$.^{49,50} Thus, the dielectric tensor $\varepsilon(\omega)$ can be called the response function to the incident light with energy $\hbar\omega$ and pointing vector $\mathbf{S}$. Therefore, our task is to calculate the dielectric functions of the systems for studying their linear optical properties. In order to calculate the dielectric function, we used a non-conserving independent particle. To do this, we employed the random phase approximation (RPA) or Lindhard theory within the Kohn–Sham DFT or time dependent DFT (TDDFT) by removing its frequency dependent exchange–correlation kernel. In principle the BSE is more accurate by considering the electron–hole interactions which can improve the optical results.²⁰ But the BSE is time consuming. Hence, in practice due to lengthy calculations, especially if the number of atoms in the system is large, BSE calculations are limited to small energy windows. Even though ε_2 values were calculated to be in good agreement with the experiments, the BSE results in predicting the intensity of ε_1 were underestimated.¹⁹ In this study, we restricted the accuracy of our results to the RPA to speed up the optical calculations. Since the space group of our systems is hexagonal, the rank of the dielectric tensor becomes one. Hence, $\varepsilon_{\mu\nu}(\omega) = \varepsilon_{\perp}(\omega)$ for $\mu = \nu = x = y$, $\varepsilon_{\mu\nu}(\omega) = \varepsilon_{\parallel}(\omega)$ for $\mu = \nu = z$, otherwise $\varepsilon_{\mu\nu}(\omega) = 0$. We obtained the total dielectric function by averaging the longitudinal ($\parallel$) and transverse ($\perp$) components of the dielectric constant, viz. $\varepsilon(\omega) = [\varepsilon_{\parallel}(\omega) +$

$2\varepsilon_{\perp}(\omega)/3^5$. We used the following formula to calculate the imaginary part of the dielectric tensor:

$$\mathcal{I}[\varepsilon_{\mu\nu}^{(\text{inter})}(\omega)] = \frac{4\pi^2 e^2}{\Omega m^2 \omega^2} \sum_{nn'\sigma} \int \frac{d\mathbf{k}}{(2\pi)^3} \left\{ \langle \mathbf{k}n\sigma | p_{\mu} | \mathbf{k}n'\sigma \rangle \right. \\ \left. \times \langle \mathbf{k}n'\sigma | p_{\nu} | \mathbf{k}n\sigma \rangle f_{\mathbf{k}n}(1 - f_{\mathbf{k}n'}) \delta(E_{\mathbf{k}n'} - E_{\mathbf{k}n} - \hbar\omega) \right\}, \quad (1)$$

where e (m) is the electron charge (mass), $\hbar\omega$ is the energy of the incoming light, $\Omega \left(\frac{(2\pi)^3}{\Omega} \right)$ is the volume of the (reciprocal) unit cell, $f_{\mathbf{k}n}$ is the Fermi-Dirac distribution function, $|\mathbf{k}n'\sigma\rangle$ is the crystal eigenfunction with momentum $\mathbf{k}$, spin σ and eigenvalue $E_{\mathbf{k}n}$, $\delta(E_{\mathbf{k}n'} - E_{\mathbf{k}n} - \hbar\omega)$ is the Dirac delta function, and $\langle \mathbf{k}n\sigma | p_{\mu} | \mathbf{k}n'\sigma \rangle$ is the matrix elements of the momentum operator p_{μ} . Our systems were treated non-magnetically, hence, the summation over σ gives a factor of 2. As such, eqn (1) is simplified to:

$$\mathcal{I}[\varepsilon_{\mu\nu}(\omega)] = \left(\frac{e}{\sqrt{\pi} m \omega} \right)^2 \sum_{nn'} \int d\mathbf{k} \left\{ \langle \mathbf{k}n | p_{\mu} | \mathbf{k}n' \rangle \right. \\ \left. \times \langle \mathbf{k}n' | p_{\nu} | \mathbf{k}n \rangle f_{\mathbf{k}n}(1 - f_{\mathbf{k}n'}) \delta(E_{\mathbf{k}n'} - E_{\mathbf{k}n} - \hbar\omega) \right\}, \quad (2)$$

where the Dirac delta function $\delta(E_{\mathbf{k}n'} - E_{\mathbf{k}n} - \hbar\omega)$ is defined as

$$\lim_{t \rightarrow \infty} \frac{1}{\pi} \frac{2\hbar}{|E_{\mathbf{k}n'} - E_{\mathbf{k}n} - \hbar\omega|^2 t} \sin^2 \left(\frac{(E_{\mathbf{k}n'} - E_{\mathbf{k}n} - \hbar\omega)t}{2\hbar} \right) \text{ which can}$$

be obtained from the well-known formula $\delta(x) = \lim_{\alpha \rightarrow \infty} \frac{1}{\pi} \frac{\sin^2 \alpha x}{\alpha x^2}$

with $x = E_{\mathbf{k}n'} - E_{\mathbf{k}n} - \hbar\omega$ and $\alpha = \frac{t}{2\hbar}$. $\mathcal{R}[\varepsilon(\omega)] = 1 + \mathcal{R}[\varepsilon^{(\text{inter})}(\omega)]$, because $\delta_{\mu\nu}$ represents an identity matrix. The real part of the dielectric function, $\mathcal{R}[\varepsilon(\omega)]$, is obtained by substituting eqn (2) into the Kramers-Kronig formula which relates the imaginary part of a complex function to its real part and *vice versa*:

$$\mathcal{R}[\varepsilon(\omega)] = 1 + \frac{2}{\pi} \mathcal{P} \int_0^{\infty} \frac{\omega' \omega' \mathcal{I}[\varepsilon(\omega')]}{\omega'^2 - \omega^2}, \quad (3)$$

where symbol “ $\mathcal{P}$ ” stands for the Cauchy principle part of the integral. The Dirac delta function is also presented in eqn (3) through the $\mathcal{I}[\varepsilon(\omega')]$ in the integrand. The delta function is there for the purpose of energy conservation, and moreover in our practical calculations was substituted by a Lorentzian function with finite broadening. The other optical properties can be straightforwardly obtained from eqn (2) and (3). In Section 4.4, we discuss our calculated index of refraction, $N(\omega) = \mathcal{R}[N(\omega)] + i\mathcal{I}[N(\omega)] = n + ik$, where n is the index of refraction and k is the extinction coefficient. $N(\omega)$ is related to the complex dielectric function as $\varepsilon(\omega) = N^2(\omega)$. If, for simplicity, we represent the dielectric function as $\varepsilon(\omega) = \mathcal{R}[\varepsilon(\omega)] + i\mathcal{I}[\varepsilon(\omega)] = \varepsilon_1 + i\varepsilon_2$, then from $\varepsilon(\omega) = N^2(\omega)$, we have $\varepsilon_1 + i\varepsilon_2 = n^2 - k^2 + 2ink$. Hence, $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$. The latter relations can be solved to obtain the index of refraction n and the extinction coefficient k . In Section 4.4, we substitute eqn (2) and (3) into the following formulas to calculate $\mathcal{R}[N(\omega)]$ and $\mathcal{I}[N(\omega)]$:

$$\mathcal{R}[N(\omega)] = \sqrt{\frac{|\varepsilon(\omega)| + \mathcal{R}[\varepsilon(\omega)]}{2}}, \quad (4)$$

$$\mathcal{I}[N(\omega)] = \sqrt{\frac{|\varepsilon(\omega)| - \mathcal{R}[\varepsilon(\omega)]}{2}}, \quad (5)$$

where $|\varepsilon(\omega)| = \sqrt{(\mathcal{R}[\varepsilon(\omega)])^2 + (\mathcal{I}[\varepsilon(\omega)])^2}$. The Dirac delta functions are present in eqn (4) and (5) and $|\varepsilon(\omega)|$ through $\mathcal{R}[\varepsilon(\omega)]$ and $\mathcal{I}[\varepsilon(\omega)]$. In Section 4.5, we report our calculated real reflectance, $R(\omega)$. The reflectance can be related to the complex index of refraction as $R(\omega) = \left| \frac{N(\omega) - 1}{N(\omega) + 1} \right|^2$, and thereby to the index of refraction and the extinction coefficient as $R = \left| \frac{n - 1 + ik}{n + 1 + ik} \right|^2$. As such, the reflectance can be calculated by substituting eqn (4) and (5) into the following formula:

$$R(\omega) = \frac{(\mathcal{R}[N(\omega)] - 1)^2 + (\mathcal{I}[N(\omega)])^2}{(\mathcal{R}[N(\omega)] + 1)^2 + (\mathcal{I}[N(\omega)])^2}. \quad (6)$$

Hence, in Section 4.5 we calculate the reflectance, as expressed in eqn (6), from the key dielectric quantity using eqn (2)–(6). The energy-loss function (ELF) is related to the dielectric function by the $\text{ELF}(\omega) = \mathcal{I} \left[\frac{-1}{\varepsilon(\omega)} \right]$ relation. Hence, it reads:

$$\text{ELF}(\omega) = \mathcal{I} \left[\frac{-1}{\varepsilon(\omega)} \right] = \frac{\mathcal{I}[\varepsilon(\omega)]}{(\mathcal{R}[\varepsilon(\omega)])^2 + (\mathcal{I}[\varepsilon(\omega)])^2}. \quad (7)$$

As such, in Section 4.6 we calculate the energy-loss function (ELF) by substituting eqn (2) and (3) into eqn (7) for the systems under study and compare our calculated ELF(ω) with the available experimental data.

4.2 Imaginary parts of dielectric functions and optical interband transitions

The imaginary parts of the dielectric functions, $\mathcal{I}[\varepsilon(\omega)]$, were calculated for the ideal $\gamma\text{-Al}_2\text{O}_3$ compound, and the defective $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$ and $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$ compounds within PBE-GGA and TB-mBJ using eqn (2) and plotted against the energy of the incident photons $E = \hbar\omega$ in the left panel of Fig. 4. If these systems are subjected to an electromagnetic field and the energies of the incident photons are lower than the bandgaps of the systems, then it is expected that the incident low energy photons cannot excite any electrons from the valence bands into the conduction bands. In this case, no absorption can take place. Thus, our calculated $\mathcal{I}[\varepsilon(\omega)]$ functions should be zero at energies lower than the bandgaps of the systems. Indeed, a $\mathcal{I}[\varepsilon(\omega)]$ curve starts to rise up at $E = E_g$, where E_g is the bandgap. This can be clearly seen in Fig. 4 with no need to shift the curves towards higher energies, as our calculated bandgaps are close to the experimental data. As such, the TB-mBJ- $\mathcal{I}[\varepsilon(\omega)]$ gives $E_g = 8.02$ eV for the ideal $\gamma\text{-Al}_2\text{O}_3$ compound, see Fig. 4(a). This is close to the experimental value⁴⁵ of 8.7 eV. The TB-mBJ- $\mathcal{I}[\varepsilon(\omega)]$ curves start to rise up at 6.6 eV in Fig. 4(b) for $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$ and at 6.7 eV in Fig. 4(c) for $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$. As such, TB-mBJ- $\mathcal{I}[\varepsilon(\omega)]$ predicted lower bandgaps for $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$ and $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$ compared to the ideal $\gamma\text{-Al}_2\text{O}_3$. This verifies that the formation of the oxygen vacancies can generate extra subbands inside the

bandgap below the CBM within TB-mBJ. Similar to TB-mBJ, PBE-GGA also predicted a lower bandgap for the compound in the presence of the neutral intrinsic point defects compared to that of the ideal structure, see the starting points of Fig. 4(a–c). Although the bandgap predicted by PBE-GGA is much smaller than that of TB-mBJ, the same trend can be clearly observed within PBE-GGA by comparing Fig. 4(a–c). In order to make it more clear, the PBE-GGA spectra were shifted by the difference between the TB-mBJ and PBE-GGA bandgaps. In this case, the first non-zero rising up points of the PBE-GGA spectra coincide with those of TB-mBJ, as shown in the right panel of Fig. 4. It is worth mentioning that in materials with strong bound excitons such as organic semiconductors the optical gap, the light absorption threshold (neutral excitation) at the difference of photoemission (charged excitation), may not be the same as the electronic or transport gap, the threshold for creating an electron–hole pair that is not bound together – the optical gap is usually lower than the electronic gap. In most inorganic materials such as our cases, there are not very strong interactions between the electrons and holes. Thus, here we have assumed that the optical band gap is approximately the same as the electronic gap due to the small exciton binding. As can be clearly seen in Fig. 4, the intensities of TB-mBJ are lower than those of PBE-GGA. It should be noticed that the intensities of

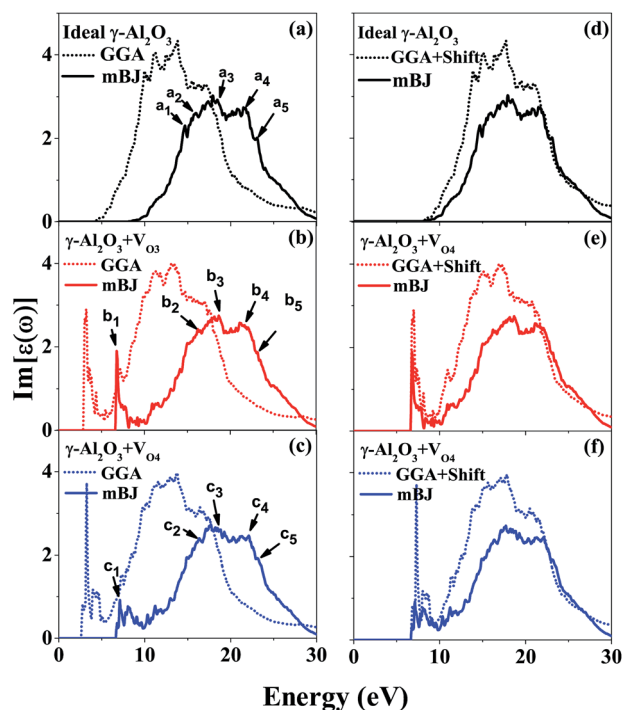


Fig. 4 The calculated imaginary part of the dielectric function, $\mathcal{I}[\varepsilon(E)]$, with respect to the energy in eV within PBE-GGA (dotted curve) and TB-mBJ (solid curve) for the (a) ideal γ - Al_2O_3 where peaks are indicated by a_i ($i = 1$ to 5), (b) γ - $\text{Al}_2\text{O}_3 + \text{V}_{\text{O}3}$ where peaks are indicated by b_i ($i = 1$ to 5), and (c) γ - $\text{Al}_2\text{O}_3 + \text{V}_{\text{O}4}$ where peaks are indicated by c_i ($i = 1$ to 5). In the right panel figures (d)–(f) the PBE-GGA spectra of the corresponding left panel figures (a)–(c) are shifted towards higher energies by the difference between the TB-mBJ and PBE-GGA bandgaps.

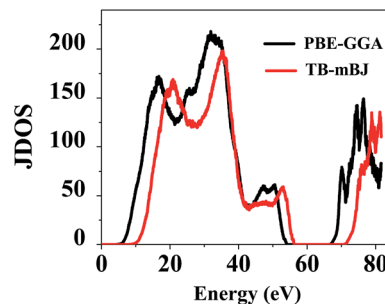


Fig. 5 The calculated joint DOS (JDOS), with respect to the energy in eV within PBE-GGA and TB-mBJ for ideal γ - Al_2O_3 . JDOSs are obtained from eqn (2) but with all matrix elements set to one.

the spectra after shifting could not be compared in details, since the Thomas–Reiche–Kuhn sum rule (f -sum rule) should be satisfied by the oscillator strength of a transition from a lower state to an upper state. Here, only an overall comparison was made without comparing the positions of the peaks of the spectra, because the intensity of PBE-GGA is visibly higher than that of TB-mBJ. At first glance it may be thought that the reason for this issue lies in the denominator of $\mathcal{I}[\varepsilon(E)]$ (see eqn (2)) the Dirac delta function as defined in Section 4.1. Since, TB-mBJ gives a larger bandgap and thereby larger a “ $E_{\text{kn}'} - E_{\text{kn}} - \hbar\omega$ ” factor than PBE-GGA, the denominator of the Dirac delta function as appeared in the predicted $\mathcal{I}[\varepsilon(E)]$ spectrum by TB-mBJ is larger than that of PBE-GGA. Consequently, it seems sensible to say that the TB-mBJ $\mathcal{I}[\varepsilon(E)]$ spectrum is lower than the PBE-GGA $\mathcal{I}[\varepsilon(E)]$ spectrum. However, on closer examination, it was observed that the numerator of $\mathcal{I}[\varepsilon(E)]$ had a more significant effect on the intensity of the $\mathcal{I}[\varepsilon(E)]$ spectrum. In order to elaborate the effect of the numerator, optical or joint density of states (JDOS) spectrum for the ideal case within PBE-GGA and TB-mBJ was plotted (see Fig. 5). The JDOS was calculated by means of eqn (2), but by setting all matrix elements to unity. Thus, we could easily investigate the effects of the denominator on the intensity of each optical spectrum. Fig. 5 shows that the intensities of PBE-GGA and TB-mBJ are fairly the same. This shows that the higher intensities can be mainly attributed to the matrix elements of the linear momentum operator. Therefore, it is shown that TB-mBJ improves the bandgap, but on the other hand it changes the matrix elements of the momentum operator; and it is the underlying reason for the presence of a big difference between the intensities of TB-mBJ and PBE-GGA.

Apart from the different heights of the PBE-GGA and TB-mBJ spectra, the energies at which their associated peaks occur seem not to be very different from each other. Despite these agreements, in this section we prefer to use our TB-mBJ results for the $\mathcal{I}[\varepsilon(\omega)]$ discussion, since in this case the predicted transition energies were obtained without shifting the $\mathcal{I}[\varepsilon(\omega)]$ spectra to adjust their starting points with the corresponding bandgaps. However, in some of the subsequent sections, we examine the abilities of PBE-GGA and TB-mBJ in reproducing the optical properties of the system by comparing their predicted results with those of the available experimental data. In this way, if the

PBE-GGA results due to their higher intensities are found in better agreement with the experiments than those of TB-mBJ due to their lower intensities, it is important to keep in mind that the calculated $\mathcal{J}[\varepsilon(\omega)]$ by PBE-GGA always needs a manual help to be shifted towards higher energies due to its well-known shortcomings in reproducing the experimental bandgap, which may not be the case for the TB-mBJ $\mathcal{J}[\varepsilon(\omega)]$. Even in this case, it is safer to evaluate the successes of PBE-GGA with predictions of those results which are related to $\mathcal{J}[\varepsilon(\omega)]$ after the required handmade shift. Let us consider the TB-mBJ $\mathcal{J}[\varepsilon(\omega)]$ spectra by beginning with the ideal case. The $\mathcal{J}[\varepsilon(\omega)]$ spectrum of the ideal case, see Fig. 4(a), shows that the probability of transition steeply increases as photon energy reaches the bandgap 8.02 eV up to 14.70 eV. Five peaks are labeled in the [14.70, 23.06 eV] energy interval by a_i ($i = 1$ to 5) in Fig. 4(a) for the ideal γ -Al₂O₃. The energies of these peaks are presented in Table 2. From point a_5 the spectrum steeply declines to reach zero. Each of these energies corresponds to an allowed transition. The transitions permitted by the selection rules are listed in Table 1. The energy of point a_1 can be attributed to the $A_8 \rightleftharpoons A_2$ transition, see Table 2. The energies of conduction, peak A_2 , and valence, peak A_8 , from the PDOS shown in Fig. 3(a) and (e) were found and are listed in Table 2. The energy difference between peaks A_2 and A_8 , i.e., $|\Delta E_{v \rightleftharpoons c}| = E_c - E_v$, was obtained to be almost identical to the energy of peak a_1 in $\mathcal{J}[\varepsilon(\omega)]$, (see Table 2). The $A_8 \rightleftharpoons A_2$ transition itself is attributed to a transition between the $O|p\rangle$ and $Al|s\rangle$ states, see Fig. 3(a) and (e) and Table 2. The $O|p\rangle \rightleftharpoons Al|s\rangle$ transition with $\Delta l = \pm 1$ is among the permissible interband transitions for ideal γ -Al₂O₃, as listed in Table 1. Hence, $O|p\rangle \rightleftharpoons Al|s\rangle$ is not only a permitted transition principally by selection rules but also a transition which can take place practically according to our calculated optical spectrum $\mathcal{J}[\varepsilon(\omega)]$. As can be seen from Fig. 4(a), our TB-mBJ $\mathcal{J}[\varepsilon(\omega)]$ distribution function of the ideal case predicts that the probability of the a_3 interband transition is maximal among the other permissible interband transitions. The a_3 point which is attributed to $A_8 \rightleftharpoons A_3$ corresponds to the $O|p\rangle \rightleftharpoons Al|s\rangle$ interband transition with $\Delta l = \pm 1$ (see Fig. 4(a), 3(a) and (e) as well as Tables 1 and 2). The remaining three transition states and their corresponding energies are listed in Table 2. Now let us consider the TB-mBJ $\mathcal{J}[\varepsilon(\omega)]$ spectra of the intrinsic defective γ -Al₂O₃ + V_{O3} and γ -Al₂O₃ + V_{O4} compounds. We detected five peaks in V_{O3} $\mathcal{J}[\varepsilon(\omega)]$ labeled by b_i ($i = 1$ to 5), see Fig. 4(b), and five peaks in V_{O4} $\mathcal{J}[\varepsilon(\omega)]$ labeled by c_i ($i = 1$ to 5), see Fig. 4(c). The energies of these peaks which were confirmed to be relevant by the partial DOSs given in Fig. 3(f–j) for γ -Al₂O₃ + V_{O3} and given in Fig. 3(k–o) for γ -Al₂O₃ + V_{O4} are listed in Table 2. Obviously, whether they were permitted transitions was also checked by considering the transitions listed in Table 1. Then, the b_i and c_i peaks for $i = 1$ to 5 were corresponded to the relevant permissible transitions and eventually presented in Table 2. If we compare the $\mathcal{J}[\varepsilon(\omega)]$ spectrum of the γ -Al₂O₃ + V_{O3} (γ -Al₂O₃ + V_{O4}) compound with that of the ideal case, we observe an obvious difference between them, by comparing Fig. 4(a) and (b) ((a) and (c)). The difference is that a sharp peak marked by b_1 (c_1) is created at low energy in the $\mathcal{J}[\varepsilon(\omega)]$ spectrum of the γ -Al₂O₃ + V_{O3} (γ -Al₂O₃ + V_{O4}) compound. This peak is created by

V_{O3} (V_{O4}), since it is absent in the $\mathcal{J}[\varepsilon(\omega)]$ spectrum of the ideal case. It is evident from Fig. 4(b) and (c) that the energies of the b_1 and c_1 transitions are less than the bandgap of the ideal compound, 8.02 eV, see Table 2. This shows that the generated subbands inside the bandgap below the CBM can act as trapping centers. Let us recall that the VBM and CBM belong to the ideal compound. The b_1 transition can be characterized as $b_1 \equiv B_9[O|p\rangle] \rightleftharpoons B_6[O|s\rangle] \approx |\Delta E_{v \rightleftharpoons c}^{b_1}|$ with $\Delta l = \pm 1$, see Tables 1 and 2 and Fig. 3(i) and (j) and 4(b). Similarly, the c_1 transition can be characterized as $c_1 \equiv C_9[O|p\rangle] \rightleftharpoons C_6[O|s\rangle] \approx |\Delta E_{v \rightleftharpoons c}^{c_1}|$ with $\Delta l = \pm 1$, see Tables 1 and 2 and Fig. 3(n) and (o) and 4(c). The characterizations show that both the b_1 and c_1 transitions take place from the $O|p\rangle$ orbital to the $O|s\rangle$ orbital. The energy of the b_1 (c_1) peak corresponds to the B_9 – B_6 (C_9 – C_6) transition energy, see Fig. 3(j) ((o)). The B_9 (C_9) state itself corresponds to the short peak (shoulder) of $O|p\rangle$ in the valence region, see Fig. 3(j) ((o)). In contrast to the A_8 peak, however, the B_9 and C_9 peaks do not correspond to the large peak of $O|p\rangle$, see Fig. 3(e), (j) and (o). The energy of $a_1 \equiv A_8[O|p\rangle] \rightleftharpoons A_2[Al|s\rangle] \approx |\Delta E_{v \rightleftharpoons c}^{a_1}|$ is less than that of a_i for $i = 2$ to 5. The required energies for b_1 and c_1 transitions are almost one-half of the required energy for the a_1 transition, viz. $E_{b_1} \leq E_{c_1} < E_g = 8.02$ eV and $E_{a_1} \approx 2E_{b_1} \approx 2E_{c_1} > E_g$ transition. Analogous to the a_i ($i = 1$ to 5) peaks, the energies of the other eight remaining b_i and c_i ($i = 2$ to 5) peaks are also larger than the bandgap of the ideal compound, see Table 2. Both of the B_9 (C_9) and B_6 (C_6) peaks are created by the V_{O3} (V_{O4}) defect, as these peaks are absent in the ideal case, as shown by comparing Fig. 3(d) and (e) with (i) and (j) ((n) and (o)). This shows that the short peak (shoulder) of $O|p\rangle$ plays an important role in the transition to the generated subbands inside the bandgap. In essence, the optical properties of the ideal compound are changed by the V_{O3} vacancy in such a way that the transition to/from the subbands generated by the intrinsic V_{O3} defect is made possible *via* the opened $b_1 \equiv B_9[O|p\rangle] \rightleftharpoons B_6[O|s\rangle]$ channel. Analogous to V_{O3}, the V_{O4} vacancy can also open a new channel of $c_1 \equiv C_9[O|p\rangle] \rightleftharpoons C_6[O|s\rangle]$ for the transition to/from the subbands generated by itself.

4.3 Real parts of dielectric functions

The real parts of the dielectric functions, $\mathcal{R}[\varepsilon(E)] \equiv \varepsilon_1(E)$, were calculated against the energy of the incident light $E = \hbar\omega$ using eqn (3) within PBE-GGA and TB-mBJ for ideal γ -Al₂O₃, and the defective γ -Al₂O₃ + V_{O3} and γ -Al₂O₃ + V_{O4} compounds. As can be seen from eqn (3), $\mathcal{R}[\varepsilon(\omega)]$ is related to $\mathcal{J}[\varepsilon(\omega)]$ through the Kramers–Kronig formula. Thus, one may expect that the $\mathcal{R}[\varepsilon(\omega)]$ spectrum calculated by PBE-GGA also needs to be shifted towards higher energies by hand compared to that of TB-mBJ. The relation between $\mathcal{R}[\varepsilon(\omega)]$ and $\mathcal{J}[\varepsilon(\omega)]$ is not linear, since the Kramers–Kronig formula is an integral equation, see eqn (3). Hence, the required shift for $\mathcal{R}[\varepsilon(\omega)]$ may not be exactly equal to the required shift for $\mathcal{J}[\varepsilon(\omega)]$. $\mathcal{R}[\varepsilon(E)]$ functions were evaluated at the static regime, $\varepsilon_1(E = 0$ eV), and at low energy, $\varepsilon_1(E = 5$ eV), as well as at high energy, $\varepsilon_1(E = 80$ eV). The results together with the available experimental data³³ and other theoretical⁵ results are presented in Table 3. The experimental data for $\varepsilon_1(E = 5$ eV) and $\varepsilon_1(E = 80$ eV) were extracted from the

experimental index of refraction ($\mathcal{R}[N(E)] \equiv n$) curve.³³ At 5 eV, $\mathcal{R}[\varepsilon(E)]$ vanishes, since this energy is less than the bandgap of the system, *viz.* 5 eV < E_g . $\mathcal{R}[\varepsilon(E)]$ also becomes zero, as the energy of the incident light approaches infinity. For such an incident light the compound becomes transparent and thereby the high energy light can go through and emerges from the system without losing its energy due to its extremely small wavelength. If $\mathcal{R}[\varepsilon(E)] = 0$, from eqn (5) we know that $\mathcal{R}[N(E)] \equiv k$ becomes zero too. Thus, at 5 eV and 80 eV $\mathcal{R}[\varepsilon(E)]$ can be extracted from the experimental index of refraction curve using the $\varepsilon_1 = n^2 - k^2 = n^2$ relation. For the latter energy, one may assume that 80 eV is such a high energy that it can be practically considered as almost the infinity limit. The results show that our calculated $\mathcal{R}[\varepsilon(E)]$ values at 5 eV using PBE-GGA are in better agreement with the experimental³³ and previous theoretical⁵ results, see Table 3. Although the results presented for $\mathcal{R}[\varepsilon(E)]$ at 80 eV in Table 3 show that the predictions of TB-mBJ are a little bit closer to the experimental value than those of PBE-GGA, this cannot resolve the problem of TB-mBJ at low energy. The static dielectric constant, $\varepsilon_1(E = 0 \text{ eV})$, increased from 3.14 to 3.55 by introducing the V_{O3} defect and to 3.56 by introducing the V_{O4} defect within PBE-GGA, see Table 3. The same trend can be seen from the calculated static dielectric constant within TB-mBJ. This trend is reversed at the low energy of 5 eV within both PBE-GGA and TB-mBJ, as can be seen by comparing $\varepsilon_1(E = 5 \text{ eV})$ of the ideal case with those of the defective cases. In contrast with the static and low energy behavior, $\mathcal{R}[\varepsilon(E)]$ changes by introducing neither the V_{O3} nor the V_{O4} defect at 80 eV, *i.e.*, $\varepsilon_1(E = 80 \text{ eV})$ remains unchanged, see Table 3. From the table, it seems that $\varepsilon_1(E = 5 \text{ eV})$ of the $\gamma\text{-Al}_2\text{O}_3 + V_{O4}$ compound, 3.36, is closer to the experimental value of 3.45. In addition to the above discussed low- and high-energy limits, $\mathcal{R}[\varepsilon(E)]$ values as the dispersive parts of the dielectric functions are plotted a function of incident light energy from 0 to 55 eV in Fig. 6(a–c) for ideal $\gamma\text{-Al}_2\text{O}_3$, and the defective $\gamma\text{-Al}_2\text{O}_3 + V_{O3}$ and $\gamma\text{-Al}_2\text{O}_3 + V_{O4}$ compounds, respectively. From these figures, it is evident that the real part of the dielectric function, as expected, asymptotically approaches unity as the energy approaches infinity, *viz.* $\lim_{E \rightarrow +\infty} \mathcal{R}[\varepsilon(E)] = 1$. However, in reality it is hard to reach the correct limit due to an imperfect convergence of the band sums in the calculation. Fig. 6 also reveals that the TB-mBJ $\mathcal{R}[\varepsilon(E)]$ asymptotically coincides with the PBE-GGA $\mathcal{R}[\varepsilon(E)]$ as the energy approaches infinity. The $\mathcal{R}[\varepsilon(E)]$ shows a positive maximum (two positive maxima) and a negative minimum for the ideal $\gamma\text{-Al}_2\text{O}_3$ compound (defective $\gamma\text{-Al}_2\text{O}_3 + V_{O3}$ and $\gamma\text{-Al}_2\text{O}_3 + V_{O4}$ compounds) within both PBE-GGA and TB-mBJ. However, the maxima and minima predicted by PBE-GGA do not occur at those energies which are predicted by TB-mBJ. Here again similar to the PBE-GGA $\mathcal{R}[\varepsilon(E)]$, the PBE-GGA $\mathcal{R}[\varepsilon(E)]$ needs to be shifted towards higher energies so that the PBE-GGA and TB-mBJ maxima and minima coincide with each others. The need of the $\mathcal{R}[\varepsilon(E)]$ shift is consistent with the anticipation indicated in the beginning of this section. The shift of the imaginary part of the dielectric function obtained from DFT calculations is always performed, because its starting point is related to the bandgap of the system, and regular DFT cannot predict the bandgap properly. The starting point of the real part of the dielectric function is not related to the bandgap of the system and thereby $\mathcal{R}[\varepsilon(E)]$ usually is not shifted. However, $\mathcal{R}[\varepsilon(E)]$ should be also shifted if it is calculated by the DFT + PBE-GGA, since $\mathcal{R}[\varepsilon(E)]$ is related to $\mathcal{I}[\varepsilon(E)]$ by the Kramers–Kronig relation. The $\mathcal{R}[\varepsilon(E)]$ of the ideal case becomes negative in an energy interval within PBE-GGA. The energy intervals of the negative regions depend on the methods used and the type of the intrinsic point defects, see Fig. 6. In the negative regions, the extinction coefficient becomes larger than the index of refraction, *viz.* $n < k$ (see eqn (4) and (5)). In this region, the percentage of reflectance increases, see eqn (6). Thus, PBE-GGA predicts that the presence of V_{O3} and V_{O4} defects causes the latter phenomena to occur at lower energies compared to the ideal case, whereas TB-mBJ inversely predicts that it occurs at higher energies.

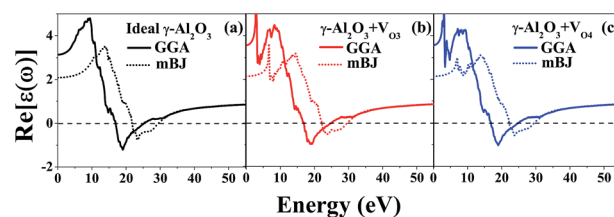


Fig. 6 The calculated real part of dielectric function, $\mathcal{R}[\varepsilon(E)]$, with respect to the energy in eV within PBE-GGA (solid curve) and TB-mBJ (dotted curve) for (a) ideal $\gamma\text{-Al}_2\text{O}_3$, (b) $\gamma\text{-Al}_2\text{O}_3 + V_{O3}$, and (c) $\gamma\text{-Al}_2\text{O}_3 + V_{O4}$. $\mathcal{R}[\varepsilon(E)]$ approaches unity as the energy becomes infinitely high, *viz.* $\lim_{E \rightarrow +\infty} \mathcal{R}[\varepsilon(E)] = 1$.

Table 3 The real part of the dielectric function, $\mathcal{R}[\varepsilon(E)] \equiv \varepsilon_1(E)$, evaluated at $E = 0 \text{ eV}$, $E = 5 \text{ eV}$, and $E = 80 \text{ eV}$ together with available experimental data and other theoretical results for comparison. $\mathcal{R}[\varepsilon(E)]$ approaches unity as the energy becomes infinitely high, *viz.* $\lim_{E \rightarrow +\infty} \mathcal{R}[\varepsilon(E)] = 1$

Method	Approx.	$\varepsilon_1(E = 0)$	$\varepsilon_1(E = 5 \text{ eV})$	$\varepsilon_1(E = 80 \text{ eV})$
Ideal $\gamma\text{-Al}_2\text{O}_3$				
FP-APW + lo	PBE-GGA	3.14	3.76	0.87
FP-APW + lo	TB-mBJ	2.08	2.19	0.90
FP-LMTO ^a	HL-LDA	3.00	3.62	0.44
$\gamma\text{-Al}_2\text{O}_3 + V_{O3}$				
FP-APW + lo	PBE-GGA	3.55	3.33	0.87
FP-APW + lo	TB-mBJ	2.13	2.34	0.90
$\gamma\text{-Al}_2\text{O}_3 + V_{O4}$				
FP-APW + lo	PBE-GGA	3.56	3.36	0.87
FP-APW + lo	TB-mBJ	2.13	2.31	0.90

Experiment^b 3.45 0.96

^a Ref. 5. ^b Ref. 33.

4.4 Complex refractive index

The index of refraction, $\mathcal{R}[N(E)] \equiv n$, was calculated using eqn (4) within PBE-GGA and TB-mBJ for the compounds in question. $\mathcal{R}[N(E)]$ was evaluated at zero, and 5 eV as well 80 eV and the results together with the available experimental data³³ and other

theoretical results⁵ are presented in Table 4. The table shows that our calculated $\mathcal{R}[N(E)]$ values using PBE-GGA at 5 eV are in better agreement with the experimental³³ and previous theoretical results.⁵ The static index of refraction, $n(E = 0 \text{ eV})$, increases from 1.77 to 1.88 for the $\text{V}_{\text{O}3}$ defect and to 1.89 for the $\text{V}_{\text{O}4}$ defect within PBE-GGA, as shown in Table 4. This trend is not changed by TB-mBJ for the static regime. However, this trend does not remain unchanged at 5 eV within both PBE-GGA and TB-mBJ. On the contrary, at high energies $\mathcal{R}[N(E = 80 \text{ eV})]$ is not changed by the $\text{V}_{\text{O}3}$ or $\text{V}_{\text{O}4}$ defect. From Table 4, it is evident that $n(E = 5 \text{ eV})$ of the $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$ compound within PBE-GGA, 1.83, is closer to the experimental value of 1.86. We have also presented our calculated $\mathcal{R}[N(E)]$ results together with experimental $\mathcal{R}[N(E)]$ curves in terms of the incident light energy from 0 to 50 eV in the left panel of Fig. 7. The PBE-GGA results show good agreement with the experiments. The extinction coefficients, $\mathcal{I}[N(E)] \equiv k$, were calculated using eqn (5) within PBE-GGA and TB-mBJ for the compounds under consideration, and are shown in the right panel of Fig. 7. The overall behavior of the extinction coefficients is comparable to that of the imaginary parts of the dielectric functions, as can be seen from Fig. 4 and the right panel of Fig. 7. Of course, their behavior in detail is not identical as the extinction coefficients depend on both the imaginary and real parts of the dielectric functions according to eqn (5). Similarly, the overall behavior of the index of refraction is close to the behavior of the real parts of the dielectric functions, see Fig. 6 and the left panel of Fig. 7. Here, we should also notice that the index of refraction depends on both the real and imaginary parts of the dielectric functions through eqn (4), and thereby cannot be exactly identical to only the real part of the dielectric function. It is worth noting that both the $\mathcal{R}[N(E)]$ and $\mathcal{I}[N(E)]$ spectra predicted by PBE-GGA need to be shifted towards higher energies to rectify the PBE-GGA drawback in reproducing the experimental bandgap. Therefore, the suitability of PBE-GGA in reproducing the

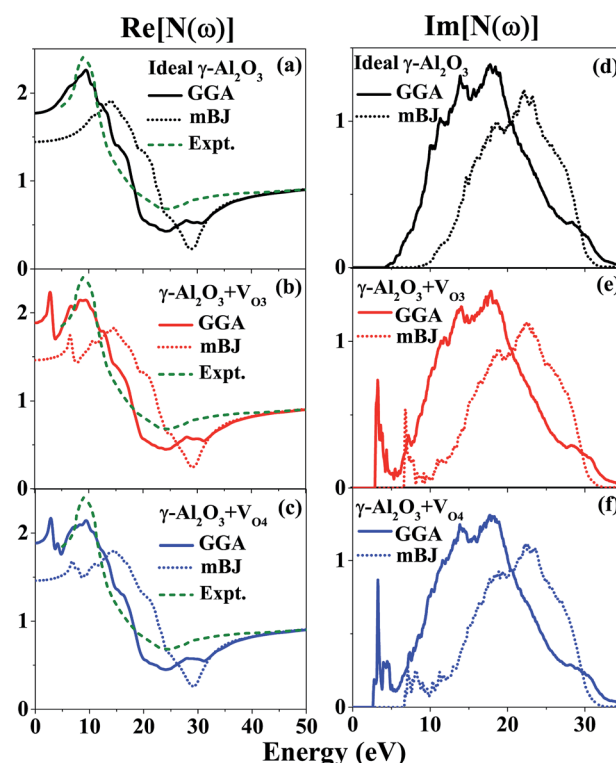


Fig. 7 The calculated index of refraction, $\mathcal{R}[N(E)]$, with respect to the energy in eV within PBE-GGA (solid curve) and TB-mBJ (dotted curve) for (a) ideal $\gamma\text{-Al}_2\text{O}_3$, (b) $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$, and (c) $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$. $\mathcal{R}[N(E)]$ approaches unity as energy becomes infinitely high, viz. $\lim_{E \rightarrow +\infty} \mathcal{R}[N(E)] = 1$. The calculated extinction coefficient, $\mathcal{I}[N(E)]$, with respect to the energy in eV within PBE-GGA (dotted curve) and TB-mBJ (solid curve) for (a) ideal $\gamma\text{-Al}_2\text{O}_3$, (b) $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$, and (c) $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$. The experimental $\mathcal{R}[N(E)]$, as shown in the left panel, figures (a)–(c), by green dashed curves, were extracted from previous work.³³

Table 4 The index of refraction, $\mathcal{R}[N(E)] \equiv n$, evaluated at $E = 0 \text{ eV}$, $E = 5 \text{ eV}$, and $E = 80 \text{ eV}$ together with available experimental data and other theoretical results for comparison. $\mathcal{R}[N(E)] \equiv n$ approaches unity as the energy becomes infinitely high, viz. $\lim_{E \rightarrow +\infty} \mathcal{R}[N(E)] = 1$

Method	Approx.	$n(E = 0)$	$n(E = 5 \text{ eV})$	$n(E = 80 \text{ eV})$
Ideal $\gamma\text{-Al}_2\text{O}_3$				
FP-APW + lo	PBE-GGA	1.77	1.93	0.93
FP-APW + lo	TB-mBJ	1.44	1.48	0.95
FP-LMTO ^a	HL-LDA	1.73	1.90	0.66
$\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$				
FP-APW + lo	PBE-GGA	1.88	1.82	0.93
FP-APW + lo	TB-mBJ	1.46	1.53	0.95
$\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$				
FP-APW + lo	PBE-GGA	1.89	1.83	0.93
FP-APW + lo	TB-mBJ	1.46	1.52	0.95
Experiment^b			1.86	0.98

^a Ref. 5. ^b Ref. 33.

experimental $\mathcal{R}[N(E)]$ is worse than that shown in the left panel of Fig. 7. However, the results show that the heights of the PBE-GGA $\mathcal{R}[N(E)]$ curves are closer to the heights of the experimental curves than those of TB-mBJ.

4.5 Reflectance

The reflectance, $R(\omega)$, was calculated using eqn (6) for the ideal and defective cases within PBE-GGA and TB-mBJ. The associated spectra are presented in Fig. 8. According to eqn (6) the reflectance depends on both the index of refraction and the extinction coefficient, and as a result on both the real and

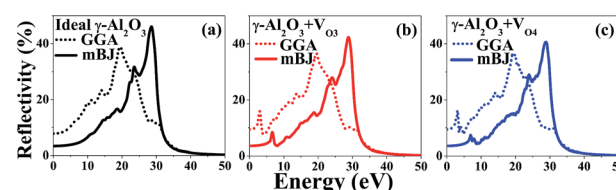
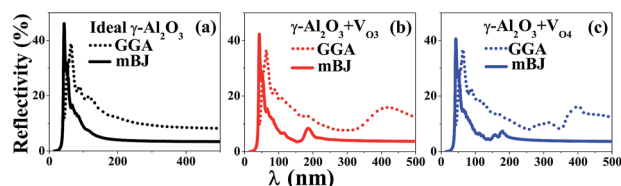


Fig. 8 The calculated percentage of reflectivity, $R(E)$, with respect to the energy in eV within PBE-GGA (dotted curve) and TB-mBJ (solid curve) for (a) ideal $\gamma\text{-Al}_2\text{O}_3$, (b) $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$, and (c) $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$.

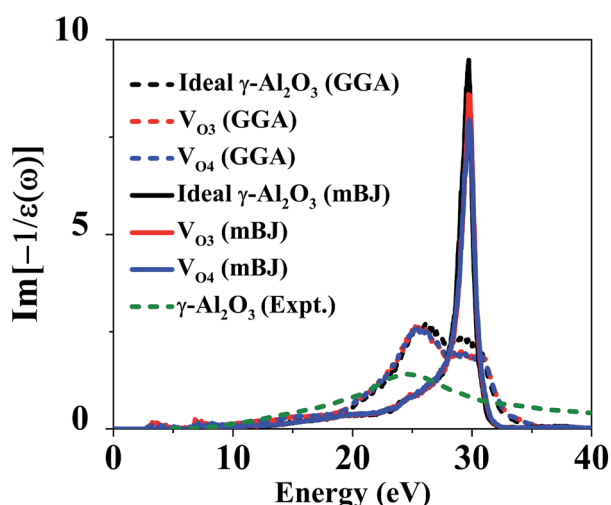
Table 5 The maximum of reflectivity, $R_{\text{MAX}}(\lambda)$, and its corresponding wavelength, λ

	Ideal $\gamma\text{-Al}_2\text{O}_3$		$\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$		$\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$	
Approx.	GGA	mBJ	GGA	mBJ	GGA	mBJ
λ (nm)	65.00	43.26	63.26	42.77	65.43	42.72
$R_{\text{MAX}}(\lambda)\%$	40.00	48.00	38.54	43.66	37.49	41.30
$\lim_{\lambda \rightarrow \infty} R(\lambda)\%$	7.77	3.31	9.45	3.53	9.42	3.51

**Fig. 9** The calculated percentage of reflectivity, $R(\lambda)$, with respect to the wavelength in nanometers within PBE-GGA (dotted curve) and TB-mBJ (solid curve) for (a) ideal $\gamma\text{-Al}_2\text{O}_3$, (b) $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$, and (c) $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$.**Table 6** The maximum of energy loss function, $\text{ELF}_{\text{MAX}}(E)$, and its corresponding energy, E

	Ideal $\gamma\text{-Al}_2\text{O}_3$		$\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$		$\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$	
Approx.	GGA	mBJ	GGA	mBJ	GGA	mBJ
E (eV)	26.10	29.72	25.50	29.70	25.30	29.78
$\text{ELF}_{\text{MAX}}(E)$	2.70	9.47	2.64	8.59	2.61	7.94

imaginary parts of the dielectric functions, see eqn (4)–(6). Our results show that the values of reflectance are large at those energy intervals for which the values of the imaginary parts of

**Fig. 10** The calculated electron energy loss function, $\mathcal{I}[-1/\epsilon(E)]$, with respect to the energy in eV within PBE-GGA (dotted curve) and TB-mBJ (solid curve) for ideal $\gamma\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$, and $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$. The experimental electron energy loss function, as shown in this figure by a green dashed curve, is extracted from French and coworkers' paper.³³

the dielectric functions are also high as well. Both PBE-GGA and TB-mBJ predict the existence of some peaks in the $R(E)$ spectra in the energy interval of $[0, E_g]$ for the defective cases. These peaks which are absent for the ideal compound originate from the subbands produced by the $\text{V}_{\text{O}3}$ and $\text{V}_{\text{O}4}$ vacancies. This prediction can be traced back to the imaginary parts of the dielectric functions where similar peaks can also be seen in the $\mathcal{I}[\epsilon(E)]$ spectra in $[0, E_g]$, see Fig. 4. Our calculated $R(\lambda)$ versus wavelength, λ , shows that the reflectance of the ideal case reaches its maximum value of 40% at a wavelength of 65 nm within PBE-GGA, see Table 5. Our results also predict that the $R(\lambda)$ curves, as shown in Fig. 9, will asymptotically go down and become constant values as the wavelength approaches infinity. These asymptotic constant values are also given in Table 5 for the cases under consideration within PBE-GGA and TB-mBJ. The constant value is calculated to be 7.77% for the ideal case within PBE-GGA. The $\text{V}_{\text{O}3}$ and $\text{V}_{\text{O}4}$ vacancies have caused the asymptotic $R(\lambda \rightarrow \infty)$ value of the ideal case to increase to 9.45% and 9.42% within PBE-GGA, respectively. Although the asymptotic values predicted by TB-mBJ are almost half of the asymptotic values predicted by PBE-GGA, the same trend as PBE-GGA can be seen in the table for the effects of the vacancies within TB-mBJ.

4.6 Energy loss function (ELF)

The electron energy-loss functions (ELFs) were calculated using eqn (7) for the ideal and defective cases within PBE-GGA and TB-mBJ. The results together with the experimental ELF³³ are plotted in Fig. 10. The ELF can behave as a gauge to measure how an incident electron loses its energy after emerging from the compounds under study. The maximum ELF for the free-electron gas in which $\mathcal{I}[\epsilon(E)] = 0$ occurs at the plasma energy $E_p = \hbar\omega_p = \hbar\sqrt{4\pi N n e^2 / m_e}$, where N is the number of atoms per unit cell, m_e is the effective mass of the electron, and n is the number of contributed valence electrons in the plasma oscillations. The E_p for Al_2O_3 was obtained⁵¹ to be 27.8 eV. Our results show that the maximum value of ELF occurs at 26.10 eV within PBE-GGA and at 29.72 eV within TB-mBJ for the ideal $\gamma\text{-Al}_2\text{O}_3$ compound, see Table 6. The experimental peak of the ELF occurs at 24.5 eV,³³ and so our PBE-GGA result for $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$, 25.30 eV, is closer to the experimental value. The results presented in Table 6 show that the plasma energy $E_p = 27.8$ eV is larger than that predicted by PBE-GGA and the experimental value but less than that predicted by TB-mBJ. The reason is that the effective masses predicted by PBE-GGA and TB-mBJ can be different from each other and from that of the free electron. The local peaks of the extinction coefficient $\mathcal{I}[N(E)]$ can be related to zeros of $\mathcal{R}[\epsilon(E)]$, compare Fig. 6 with the right panel of Fig. 7 and see eqn (5). However, the peaks of the ELF spectra occur at energies that are larger than those energies for which $\mathcal{R}[\epsilon(E)]$ becomes zero, see Fig. 6 and 10, because $\mathcal{I}[\epsilon(E)]$ is still large at these energies. If $\mathcal{R}[\epsilon(E)] = 0$, from eqn (5) we have $\mathcal{I}[N(E)] = \frac{\sqrt{2}}{2} \sqrt{\mathcal{I}[\epsilon(E)]}$ and eqn (7) can be also simplified as $\text{ELF}(E) = \mathcal{I}[-1/\epsilon(E)] = (\mathcal{I}[\epsilon(E)])^{-1}$. Therefore, from the latter inverse relation we see for the case of $\mathcal{R}[\epsilon(E)] = 0$ that the ELF can grow upwards provided that the imaginary part of the

dielectric function becomes small. The peak of the ELF occurs at 25.30 eV within PBE-GGA and at 29.78 eV within TB-mBJ for $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$, see Fig. 10 and Table 6. The PBE-GGA (TB-mBJ) $\mathcal{A}[\varepsilon(E)]$ spectrum becomes small at 25.30 eV (29.78 eV), see the left panel of Fig. 4. Therefore, the ELF spectrum grows upwards at 25.30 eV (29.78 eV) within PBE-GGA (TB-mBJ), see Fig. 10 and Table 6. This result is consistent with what we have already shown by setting $\mathcal{R}[\varepsilon(E)] = 0$ in eqn (7) for small $\mathcal{A}[\varepsilon(E)]$; viz. $\text{ELF}(E) = 1/\mathcal{A}[\varepsilon(E)]$. The PBE-GGA $\text{ELF}(E)$ results are in better agreement with the experiments. The bandgap is predicted better by TB-mBJ, but TB-mBJ fails to predict the loss function properly. In the loss function there are two main components; the first component is $\langle \mathbf{k}\mathbf{n}\sigma | p_\mu | \mathbf{k}\mathbf{n}'\sigma \rangle$ and the second component is “ $E_{\mathbf{k}\mathbf{n}'} - E_{\mathbf{k}\mathbf{n}} - \hbar\omega$ ”. The second component is related to the energy distances which are suitably produced by TB-mBJ. Therefore, we anticipate that the first component is not so suitably reproduced by TB-mBJ that it can give the loss function in complete accordance with the experiments. The matrix elements of the linear momentum operator as the first component can be well calculated, if the eigenstates of the systems are well reproduced. Thus, the problem can be attributed to the eigenstates of the system. This indicates that even though the bandgap and the positions of the subbands are well reproduced by the TB-mBJ scheme, the details of the bands in the band structures may not be better than PBE-GGA. This may also be acceptable, since TB-mBJ is designed to overcome the LDA/GGA bandgap problem.

5 Conclusions

The effects of the intrinsic O point defects on the optical properties of $\gamma\text{-Al}_2\text{O}_3$ were investigated using density functional theory utilizing the PBE-GGA and TB-mBJ-GGA functionals. Permissible transitions were categorized in our optical investigations by calculating the partial DOSs and imaginary part of the dielectric function, $\mathcal{A}[\varepsilon(\omega)]$. Among them, the probability of the $\text{O}|p\rangle \rightleftharpoons \text{Al}|s\rangle$ interband transition was found to be higher than those of the other transitions. However, after introducing oxygen vacancies, the $\mathcal{A}[\varepsilon(\omega)]$ was changed so that $\text{O}|p\rangle \rightleftharpoons \text{O}|s\rangle$ transitions could take place, where the latter states are generated by the oxygen vacancies. The distances between these states were found to be less than the bandgap of the ideal case, which indicated that the subbands generated by the oxygen vacancies can behave as trapping centers inside the bandgap of the ideal case. The oxygen defects caused the real part of the dielectric function, $\mathcal{R}[\varepsilon(E)]$, at the lowest energy to increase from 3.14 to 3.56, while $\mathcal{R}[\varepsilon(E)]$ tended to remain unchanged at energies higher than 35 eV. The index of refraction, $\mathcal{R}[N(E)]$, at $E = 0$ ($E = 5$ eV) was increased (decreased) by the oxygen defects within PBE-GGA, while it remained constant at high energies. It is noteworthy that, both $\mathcal{R}[N(E = 5 \text{ eV})]$ and $\mathcal{R}[\varepsilon(E = 5 \text{ eV})]$ were closer to the reported experimental values for the $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}4}$ as compared to those of the ideal and $\gamma\text{-Al}_2\text{O}_3 + \text{V}_{\text{O}3}$ cases. Our results demonstrate clearly that the effects of the intrinsic point defects on the electronic structure and optical properties of this compound are of significant importance. When using non-regular TB-mBJ, one does not need to shift the $\mathcal{A}[\varepsilon(\omega)]$ curve, since this method provides the band gap close to the

experimental value, which is not the case for PBE-GGA due to its poor band gap prediction. The intensities of the imaginary parts of the dielectric constants were predicted by TB-mBJ to be lower than those of PBE-GGA for the cases under study. The lower intensities are mainly attributed to the produced eigenstates and thereby to the generated matrix elements of the linear momentum operator, as discussed in detail throughout the optical properties subsections.

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