

## Electronic Supplementary Information for *Chemical Communications*

### Microscopic origin of the optical processes in blue sapphire

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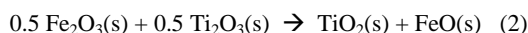
#### Computational Methods

The code GULP developed by Gale (1997) has been used to calculate the optical and defect properties of sapphire.<sup>1,2</sup> Interatomic potentials were taken from the work of Lewis and Catlow.<sup>3,4</sup> The accuracy of the model was validated by the comparison of the properties calculated with those from reference sources. The interatomic potentials included a long-range Coulombic term computed via the Ewald summation technique, and a short-range Buckingham term.

The Shell Model of Dick and Overhauser (1958) was employed in order to accurately model ionic polarisation.<sup>5</sup> The multi-region Mott-Littleton approach (1938) was then employed to calculate the interactions of the modelled defects with the surrounding lattice.<sup>6</sup> Converged sizes of 10 Å (950 ions) and 25 Å (14,278 ions) were used for regions 1 and 2, respectively. The cut-off distance for the short-range potentials was set at 15 Å.

In order to model the intervalence charge transfer process and construct the configuration coordinate diagram, two minimisation techniques are required to separate the vertical (electronic relaxation) and adiabatic (electronic and ionic relaxation) terms. The former was achieved through a “shell only” optimisation, which fixes the core of the ions but allows the shells (representing the polarisation of the valence electrons) to relax (producing point 2). The latter was achieved through a full optimisation procedure, involving the ions (and shells) being located in their local energy minima (producing points 1 and 3).

In order to calculate the net absorption energy between the configuration coordinates of the two pairs of ions, an additional alignment term is required, which accounts for the difference in ionisation potentials of the two cations:



This contribution is 2.13 eV, with the final results included in Table 1 of the manuscript.

The determination of the crystal field energies of the metal cations in sapphire (Table 2 of the manuscript) required an extension to the GULP code. The AOLM (Angular Overlap Model) developed by Woodley (2001) incorporates angular functions to purely radial inter-atomic potentials.<sup>7,8</sup> This approach allows non-spherical cations to be modelled, and their crystal field parameters to be accurately evaluated. The crystal field potentials were parameterised using reference spectra for the appropriate hexa-aqua complexes, and transferred to the corundum system. The effect of Jahn-Teller distortions were omitted, but would only be present for Ni<sup>2+</sup> assuming the cations to be in a high spin configuration, and therefore will not affect the conclusions made. Within the AOLM only intra-atomic d-d transitions were considered.

An alternative approach would be to employ a quantum mechanical technique to calculate the optical response; however, popular methods such as time-dependant density functional theory are known to fail for charge transfer excitations.<sup>9</sup> For the ground state configurations, preliminary calculations (using semi-local and non-local exchange-correlation functionals within the code VASP<sup>10</sup>) support our conclusions in relation to the equilibrium III/III configuration and the weak preference for face-sharing configurations.

1. J. D. Gale, *J. Chem. Soc.*, 1997, **93**, 629-637.
2. J. D. Gale, *Zeit. Kristall.*, 2005, **220**, 552-554.
3. C. R. A. Catlow, *Proc. Roy. Soc. A*, 1977, **353**, 533-561.
4. G. V. Lewis, *Physica B & C*, 1985, **131**, 114-118.
5. B. G. Dick and A. W. Overhauser, *Phys. Rev.*, 1958, **112**, 603.
6. C. R. A. Catlow, *Theor. Chem. Acc.*, 2000, **103**, 205-208.
7. S. M. Woodley, P. D. Battle, C. R. A. Catlow and J. D. Gale, *J. Phys. Chem. B*, 2001, **105**, 6824-6830.
8. S. M. Woodley, J. D. Gale, P. D. Battle and C. R. A. Catlow, *J. Chem. Phys.*, 2003, **119**, 9737-9744.
9. D. J. Tozer, *J. Chem. Phys.*, 2003, **119**, 12697.
10. G. Kresse and J. Furthmüller, *Comp. Mater. Sci.*, 1996, **6**, 15-50.