

Research Article

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Supplementary Material: High refractive index and extreme biaxial optical anisotropy of rhenium diselenide for applications in all-dielectric nanophotonics.

<https://doi.org/10.1515/sample-YYYY-XXXX>

Received Month DD, YYYY; revised Month DD, YYYY; accepted Month DD, YYYY

Computational details of the ab-initio modelling

We performed three main computational steps. The first one was a full optimization of the spatial structure within DFT for the relaxation of a stressed system and determination of the equilibrium configuration. We used X-ray diffraction data [4] as the starting coordinates and Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-newton algorithm for geometry optimization. We used fully relativistic pseudopotentials with the projector augmented wave (PAW) method [3] from PSLibrary [1]. Calculations were performed with convergence threshold on the total energy for ionic minimization 10^{-6} (a.u) and convergence threshold on forces for ionic minimization 10^{-5} (a.u). The Monkhorst-Pack grid 6x6x6 was used for geometry optimization. Kinetic energy cut-off corresponds to 60 Rydberg for wave functions and 300 Rydberg for charge density and potential with convergence threshold for self consistency 10^{-10} . The results of the geometry optimization and their comparison to the experimental data is summarized in Table 1.

Tab. 1: Calculated and experimental lattice parameters and angles for bulk ReX_2 systems

	a(Å)	b(Å)	c(Å)	α (°)	β (°)	γ (°)
<i>ReS₂</i>						
Exp bulk [5]	6.510	6.461	6.417	88.38	106.47	121.10
DFT bulk	6.310	6.414	6.301	91.59	105.27	118.78
<i>ReSe₂</i>						
Exp bulk [9]	6.602	6.716	6.728	91.82	104.90	118.94
DFT bulk	6.597	6.710	6.721	91.84	104.90	118.91

The second step was a self-consistent calculation of electronic structure within DFT by pw.x code as a part of QE package. This code allows to calculate ground-state energy and one-electron Kohn-Sham orbitals. For ground state the number of computed bands was equal to number of electron in the unit cell. A band structure calculation was provided by bands.x code of QE package. The number of occupied and unoccupied orbitals was equal 188 and 72 for *ReSe₂* and 108 and 42 for *ReS₂* respectively. As it was shown in the recent work [2] only generalized gradient approximation (GGA) instead of local density approximation (LDA) is convenient for band structure calculations of these systems. To check it we computed

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self-consistent calculation by two levels of DFT - LDA and GGA, and compared obtained results between themselves and with work [2]. The Perdew–Zunger [6] for the LDA and Perdew–Burke–Ernzerhof [7] for GGA exchange–correlation functionals are used. The bands was calculated for different choices of grids to cover the whole 3D BZ. This process is not usually required in more high-symmetry materials and can be computationally expensive. But as it was shown in work [2] discarding the third component of the wave vector for the bulk rhenium dichalcogenides leads to impossibility to determine whether the band extrema occur at the same crystal momentum values.

The third step was a calculation of the optical response. To describe the absorption spectra we used the linear response time dependent density functional theory (TDDFT) based on the solution of quantum Liouville equation with PBE exchange–correlation kernel as well. It allows us to calculate absorption spectra of molecules using the Lanczos recursion algorithm without computing empty states [8]. For this purpose we used turbo-lanczos.x program as a part of QE package. Physical quantities under study were the real and imaginary parts of the all component of the unit cell polarizability tensor α_{xx} , α_{yy} and α_{zz} at the Γ point. The number of Lanczos iterations was 20000 and the broadening/damping parameter was equal 25meV. All data was interpolated by cubic B-splines.

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