Research article

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

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Abstract: We establish a simple quantitative criterium for the search of new dielectric materials with high values of refractive index in the visible range. It is demonstrated, that for light frequencies below the bandgap, the latter is determined by the dimensionless parameter η calculated as the ratio of the sum of the widths of conduction and valence bands and the bandgap. Small values of this parameter, which can be achieved in materials with almost flat bands, lead to dramatic increase of the refractive index. We illustrate this rule with a particular example of rhenium dichalcogenides, for which we perform ab initio calculations of the band structure and optical susceptibility and predict the values of the refractive index $n > 5$ in a wide frequency range around 1 eV together with comparatively low losses. Our findings open new perspectives in search for the new high-index/low-loss materials for all-dielectric nanophotonics.

Keywords: ab initio calculations; all-dielectric nanophotonics; dichalcogenides; high refractive index.

1 Introduction

All-dielectric photonics [1, 2] is arguably the most rapidly evolving field of modern nano-optics. The basic component in all-dielectric photonics, a dielectric nanoantenna,

supports optical Mie resonances [3], with properties that can be flexibly controlled by the geometry of a nanoantenna. In particular, the variation of its shape allows changing the nature of the lowest energy optical resonance from electric dipole to magnetic dipole [4, 5], the functionality inaccessible in plasmonic devices. With the current stage of technology, the fabrication of specifically designed arrays of resonant antennae with finely controlled shape and lattice geometry became a routine task, which paved the way toward unprecedented control over linear [6–8] and nonlinear [9, 10] light manipulation.

The key factor defining the functionality of resonant all-dielectric nanostructures, besides their shape, is the value of the refractive index of the material forming resonant nanoantennas. Indeed, the quality factor of the fundamental Mie resonance scales is n^2 , and the ratio of the nanoantenna size to the resonant wavelength is $1/n$. Thus, the increase in the refractive index would allow for both more sharp and more deep subwavelength resonances in all-dielectric nanostructures, provided that the extinction coefficient, related to the imaginary part of the refractive index, is kept small.

While virtually purely real refractive indices $n > 10$ can be easily achieved in the wide frequency range from terahertz to mid-IR, in the near-IR and visible ranges, the values of refractive index are currently limited by a value of approximately 5. Around a characteristic photon energy of 1 eV, standard high-index reference materials are crystalline silicon ($n \approx 4$), gallium arsenide ($n \approx 3.7$), and germanium ($n \approx 4.5$). It is clear that the broadband large refractive index in this frequency range is provided by strong interband polarization. However, the questions of what are the other parameters which can contribute to high values of the off-resonant refractive index, are there any fundamental upper limit for this quantity, and whether it can be substantially increased with respect to the values characterizing current high-index materials remain unexplored to our knowledge.

In this work, we show the sum of the widths of the conduction Δ_c and valence Δ_v bands to the bandgap.

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$$\eta = \frac{\Delta_c + \Delta_v}{E_G} \quad (1)$$

is the key parameter which defines the value of the refractive index for the frequencies slightly below the bandgap. We derive a simplified estimation for the susceptibility and demonstrate that the refractive index can be substantially increased if η becomes small, as it happens in materials with flattened valence and conduction bands. This situation takes place in ReSe₂, for which we perform the ab initio analysis of the optical properties and predict that for the photon energies around 1 eV, the real part of the refractive index $n > 5$, which is the current record high value, and its imaginary part remains small. We also predict extreme biaxial optical anisotropy in this material.

2 Theoretical model

We start from considering a simplified model of interband polarization in bulk material and show that the condition of the weak dependence of the bandgap on the wave vector in the whole Brillouin zone (BZ) (the extreme case being a material with flat bands) results in a high value of optical susceptibility close to the absorption edge.

We start from the simplest expression for the susceptibility tensor given by the Kubo formula

$$\chi_{\alpha,\beta}(\omega) = \frac{\hbar}{\omega \Omega N_k} \sum_{k,m,n} \frac{f(\epsilon_{nk}) - f(\epsilon_{mk})}{\epsilon_{nk} - \epsilon_{mk}} \frac{\langle nk | j_\alpha | mk \rangle \langle mk | j_\beta | nk \rangle}{\hbar\omega - (\epsilon_{nk} - \epsilon_{mk}) + i\gamma}, \quad (2)$$

where $\alpha, \beta = x, y, z$, Ω is the unit cell volume, N_k is the number of points in the BZ, over which we make the summation, f is the Fermi–Dirac distributions, $|nk\rangle$ is the Bloch eigenfunctions for the corresponding band, and j_α is the current operators given by:

$$\hat{j} = -\frac{e}{\hbar} \nabla_k H_k, \quad (3)$$

where H_k is the hamiltonian in the basis of Bloch eigenfunctions.

Let us consider the simplest case of a cubic unit cell, for which $\Omega = D^3$, where D is the lattice period. We limit ourselves to the case of single conduction and valence bands separated by the bandgap E_G , assuming that $E_G \gg kT$ and putting $f_c = 0, f_v = 1$. We then can rewrite the expression for the susceptibility as:

$$\chi_{\alpha,\beta}(\omega) = \frac{\alpha}{(k_0 D)} \left(\frac{\hbar^2}{m_0 D^2} \right)^2 \frac{1}{N_k} \times \sum_k \frac{D^2 P_\alpha^*(k) P_\beta(k)}{[\epsilon_c(k) - \epsilon_v(k)][\hbar\omega - (\epsilon_c(k) - \epsilon_v(k)) + i\gamma]} \quad (4)$$

where $\alpha \approx 1/137$ is the fine structure constant, $k_0 = \omega/c$, m_0 is the free electron mass, and $P_\alpha(k) = \int d^3 r u_{c,k}^*(\mathbf{r}) (\partial/\partial \mathbf{r}_\alpha) u_{v,k}(\mathbf{r})$ is the matrix element of interband polarization. The presence of the prefactor $\alpha/(k_0 D)$ allows understanding why one usually observes large permittivities at longer wavelengths. Indeed for the frequency $2\pi\hbar\omega = 1$ GHz and typical unit cell size $D \approx 5.7 \times 10^{-10}$ m (lattice constant of germanium), the term $\alpha/(k_0 D)$ can be as large as 10^6 . On the other hand, in the range of optical frequencies $\hbar\omega \approx 1$ eV, $\alpha/(k_0 D) \approx 2.5$. The characteristic energy $\hbar^2/(m_0 D^2) \approx 0.5$ eV is comparable with the bandgap width.

At the first sight, it seems that the recipe for the large value of susceptibility is straightforward: if the material has $\epsilon_c(k) - \epsilon_v(k) \approx \text{const}(k) = \tilde{\epsilon}$, then tuning the frequency slightly below $\tilde{\epsilon}$, we can achieve arbitrary large susceptibility with vanishing losses. Unfortunately, this would not work so directly because conduction and valence band dispersions and matrix elements P are directly related to each other. This can be easily seen if we use $\mathbf{k} \cdot \mathbf{p}$ perturbation theory. As a very rough approximation, we can assume that the dispersion in the whole BZ is parabolic and isotropic (which of course is not the case in real materials) and write

$$\begin{aligned} \epsilon_c(k) - \epsilon_v(k) &= E_G + \hbar^2 k^2 \left(\frac{1}{2m_c} - \frac{1}{2m_v} \right) = E_G + \frac{\hbar^2 k^2}{2\mu} \\ &= E_G + \frac{\hbar^2 k^2}{2m_0} \left(\frac{4\hbar^2 |P|^2}{m_0 E_G} \right), \end{aligned} \quad (5)$$

where the last equality follows from two band $\mathbf{k} \cdot \mathbf{p}$ perturbation theory. We can see that the constant energy difference between the two bands can be achieved only if $|P|^2$ vanishes, but this means that optical transitions between valence and conduction bands are forbidden, which corresponds to zero net susceptibility. The dependence of χ on the bandwidths is therefore determined by the competition between the numerator and denominator in Eq. (4).

If we set $\hbar\omega = E_G - \delta$, $\delta \ll E_G$ and go from summation to the integration over the BZ, we can derive simple analytical expression for susceptibility:

$$\chi(\omega) \approx \frac{\alpha}{(k_{E_G} D)} \frac{1}{\pi^2} \frac{\tan^{-1}(\pi\sqrt{\eta}) - 2^{-1/2} \tan^{-1}(\pi\sqrt{\eta/2})}{\sqrt{\eta}}, \quad (6)$$

where $k_{E_G} = E_G/(\hbar c)$ and $\eta = \hbar^2/(\mu D^2 E_G) = (\Delta_c + \Delta_v)/E_G$. This simplified expression substantially underestimates the dielectric constant for real semiconductors (e.g., for GaAs, it gives the estimate for $\epsilon \approx 7$ instead of the experimental value $\epsilon \approx 13.5$). This is mainly due to the effects of nonparabolicity of the electron dispersion and neglect of the interband polarization corresponding to the higher bands. Nevertheless, Eq. (6) allows determining qualitatively the dependence of

the susceptibility on η , as it contains the universal decaying function of this parameter. Therefore, although the matrix element of the interband transition decays with decrease in η , maximal values of the susceptibility should be still expected for materials with small η , i.e., for those having large gap and narrow conduction and valence bands.

Fortunately, one can find representatives of this class of the materials, the example being bulk ReSe_2 [11]. This layered material belonging to the rhenium dichalcogenide family has been gaining recently increasing attention, mainly owing to its pronounced in-plane anisotropy and suppressed interlayer van der Waals coupling [12]. To check the results of our qualitative analysis, in the next section, we provide the data of ab initio modeling of the linear optical response of bulk ReSe_2 .

3 Results of the ab initio modeling

All ab initio calculations were performed using QUANTUM ESPRESSO package [13]. The analysis of the optical response was performed in three steps.

In the first step, we determined the equilibrium positions of the ions in the lattice by full self-consistent geometry optimization within density functional theory (DFT). The top and side views of the resulting structure are presented in Figure 1. The obtained lattice parameters and their comparison to experimental XRD data are given in Supplementary.

In the second step, we employed two different DFT approaches (LDA and GGA) to calculate the three-dimensional (3D) band structure.

In the third step, we calculated the diagonal components of the unit cell polarizability tensor α_{ii} via time-dependent DFT (TDDFT) (see details in Supplementary).

Most of the previous calculations of the band structure of the considered materials focused only on the dispersion along the special sets of directions, example being the 2D projection into the layers plane [14, 15]. In the other cases, highly symmetric paths were chosen in the 3D BZ connecting 3D special points, without exploring the structure of the whole BZ [16, 17] and thus missing the true band edges, which are crucially important for the determination of the optical response. The possible drawbacks of this approach were analyzed in detail in the recent work [11], wherein the necessity of the calculation of the band energies everywhere within the BZ and determination of the constant energy surfaces was stressed. In the present paper, we used the k -path, developed in the study by Gunasekara et al. [11], and calculated the band structure using the following path: $\text{CBM}-\text{CBM}'-\text{Z}-\Gamma-\text{VBM}-\text{VBM}'-\text{Z}-\Gamma$, where CBM is the conduction band minimum (LUMO), VBM is the valence band maximum (HOMO), and CBM' and VBM' are the intersection points of the boundary surface of the BZ and the straight lines connecting Γ and CBM or VBM points, respectively. The paths from CBM' or VBM' points to the Z point run along the surface of the BZ containing the Z point. To find the k -points corresponding to the VBM and CBM, we used the different grids in $\text{BZ}-6 \times 6 \times 6$ and $7 \times 7 \times 7$. The calculated values of the direct and indirect bandgap are presented in Table 1 and compared with the previously reported data [11, 16].

Figure 1: The unit cell, side and top views, of the ReX_2 bulk structure. The a , b , and c are crystallographic axes marking the unit cell. Rhenium and sulfur (or selenium) atoms are indicated in blue and yellow, respectively. It can be seen that the set of the elementary cells forms a quasi-two-dimensional bulk material. The x , y , z , axes are marking the cartesian coordinates system.

Table 1: Bandgap values calculated within LDA and GGA.

Type/Material	LDA/GGA	LDA [11]/ GGA [11]	GGA + GW [16]
Indirect ReSe ₂	1.0043/1.0463	0.87/0.99	–
Direct (Z) ReSe ₂	1.0714/1.0909	0.97/1.00	1.38
Direct (Γ) ReSe ₂	1.3262/1.3421	–	–
Indirect ReS ₂	1.1424/1.1790	–	–
Direct (Z) ReS ₂	1.1908/1.2147	–	1.60
Direct (Γ) ReS ₂	1.6809/1.7441	–	1.88

CBM, conduction band minimum; VBM, valence band maximum.

The grid $6 \times 6 \times 6$ was used to define the VBM point for ReSe₂ and CBM point for ReSe₂, and the grid $7 \times 7 \times 7$ was used to define the CBM point for ReSe₂ and VBM point for ReS₂. This choice was dictated by the reasons of grid parity and symmetry of the BZ. All energies are given in electron volt.

The obtained band structures of ReSe₂ and ReS₂ are presented in Figure 2. It can be seen that the energy of the lowest conduction and the highest valence bands depend only weakly on the wavevector, and the bands are close to the flat ones.

In order to get the the optical response, we employ the TDDFT approach, calculating the diagonal terms of the unit cell polarizability α_{ii} . The average dielectric susceptibility $\chi_{ii}(\omega)$ was found as the ratio of the polarization and the unit cell volume V , $\chi_{ii} = \alpha_{ii}/V$. The dielectric permittivity was then found as $\epsilon_{ii} = 1 + 4\pi\chi_{ii}$. The spectra of the dielectric permittivities are shown in Figure 3.

It can be seen that for both ReSe₂ and ReS₂, the absorption sharply increases only when the photon frequency approaches the bandgap in Γ point, 1.32 and 1.7 eV, respectively. Furthermore, we observe strong biaxial anisotropy for both crystals, stemming both from the layered structure of the material and reduced in-plane symmetry of the rhenium dichalcogenides [18]. Noteworthy, large refractive index contrast and strong uniaxial anisotropy have been recently experimentally measured in bulk transition metal dichalcogenides [19–21] and hexagonal boron nitride [22]. The pronounced biaxial anisotropy may be used for the the observation of the Dyakonov surface waves [23] in the rhenium dichalcogenide waveguides.

One can see that the real parts of the in-plane components of the permittivity of ReSe₂ exceed 25 in the broad frequency range, which should correspond to the high refractive index. Since for biaxial crystals, the refractive index depends on the light propagation direction, we limit ourselves to the case when light travels along one of the three principal axes. In this case, the refractive index for each of the two polarizations is just a square root of the corresponding permittivity. The spectra of the refractive index components are shown in Figure 4. One sees that in

Figure 2: The band structure of the bulk ReSe₂ and ReS₂ calculated by the GGA level of DFT for the path going through Γ and Z points and the band extrema (CBM and VBM). The Fermi energy is set to zero. The CBM' and VBM' points are the intersection points of the boundary surface of the BZ and the straight lines connecting the Γ point and CBM or VBM points, respectively. The bands are flattened in a wide range of the wave vectors. CBM and VBM points correspond to the different k -values, so this is an indirect semiconductor. CBM, conduction band minimum; VBM, valence band maximum; DFT, density functional theory.

the broad wavelength range, the refractive index exceeds 5, which is substantially larger than the index of the modern state-of-the-art high-index materials such as c-Si [24], GaP [25], and Ge [26]. The refractive index of ReS₂ is smaller than that of ReSe₂, but is still quite large. It should be noted that the imaginary part of the refractive index in this wavelength range is negligibly small.

In our analysis, we have not accounted for the excitonic contribution to the dielectric permittivity, which can be substantial and would lead to the additional absorption losses at the frequencies slightly below the bandgap. Nevertheless, since the range of the large refractive index covers more than 0.5 eV below the bandgap, it should be possible to detune from the exciton absorption lines to probe the lossless large refractive index.

Figure 3: Real and imaginary parts of ϵ of the bulk ReSe_2 (left) and ReS_2 (right) for different light polarizations calculated within TDDFT (see details of calculations in Supplementary). It can be seen that the peaks of the imaginary part of the permittivity, and hence the absorption edges, are 1.32 eV for ReSe_2 and 1.7 eV for ReS_2 . TDDFT, time-dependent density functional theory.

Figure 4: The calculated dependence of the the real and imaginary parts of refractive indexes of ReSe_2 (left) and ReS_2 (right) on the wavelength for different cases of light polarizations. The known experimental data for the modern state-of-the-art high-index materials such as c-Si [24], GaP [25], and Ge [26] are shown for comparison.

4 Conclusions

We established a simple quantitative criterium for the search of high-refractive-index dielectric materials, expressed in terms of the single dimensionless parameter calculated as the ratio of the sum of the widths of conduction and valence bands and the bandgap. With the use of it, we found that ReSe_2 is low-loss material, possessing a record high refractive index $n > 5$ in a wide frequency range around 1 eV. Our conclusion is

supported by the results of the DFT simulation of the optical response. Since currently there exist vast material databases containing the data on their band structures, the proposed criterion can be used for the automated search of the perspective candidates for the novel high-index materials for all-dielectric photonics.

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