Calculation of anisotropic reflectance of SrNbO$_{3.4}$ within Density Functional Theory

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Abstract. A recent experimental study on SrNbO$_{3.4}$ material has revealed a very pronounced anisotropy of its complex dielectric function. This material shows a metallic characteristic along $a$ crystal direction but behaves as an insulator along $b$ and $c$ crystal directions. To investigate this interesting phenomenon, we perform first-principles calculations within density functional theory, to theoretically produce the complex dielectric functions along those crystal directions, and predict the anisotropy of the corresponding reflectance. This result ensures its anisotropic optical property and can explain the unique feature of this material under exposure of electromagnetic radiation.

Keywords: Anisotropic reflectance, dielectric functions, density functional theory

1. Introduction
Among the research interests in plasmonic technology is the search of material which can be used as a good optical switch. The capability to play as a good optical switch may require a low switching power density but yet a high switching contrast. Investigations on isotropic materials such as gold (Au) show that the optical switching functionality of that material demands a high switching power density but performs a low switching contrast [1–6]. Those findings suggest that one needs to search for materials with anisotropic optical characteristics.

Rather than using isotropic materials, one can consider a material that has different optical response characteristic along each crystal direction. Materials which exhibit this feature are called the anisotropic materials, and one of them is the SrNbO$_{3+\delta}$ family. The layered perovskite-related niobates ($n = 5$) SrNbO$_{3.4}$ has been studied and found that it has an interesting optical properties. This feature is firstly recognized by the experimental study using Angle-Resolved Photoemission Spectroscopy (ARPES) which informs that perovskite-related Sr$_{1-x}$La$_x$NbO$_{3.5-x}$ has one-dimensional Fermi surface along $\Gamma$-X direction [7]. Furthermore, experimental study of its electronic and vibrational properties also show that SrNbO$_{3.41}$ and SrNbO$_{3.45}$ exhibit a metallic behavior at room temperature with strongly dispersing band along $a$ crystal direction, and insulating with non-dispersive character along $b$ direction [8]. Recently, another experimental study also reveals that under a very low power density of pump-probe microscopy, this material displays the reflectance reduction only if the pumping electric field is polarized along the $b$ crystal direction while the probing field is polarized along the $a$ crystal axis [9]. By these findings, one can conclude that the SrNbO$_{3.4}$ has a highly anisotropic property, where along $a$ crystal axis it behaves as a metal, while along $b$ and $c$ it is an insulator.
Figure 1. Crystal structure of SrNbO$_{3.4}$. The cyan balls represent the strontium atom, the gray balls represent the niobium atom and the red balls represent the oxygen atom.

Here, our study is aimed to explore the optical properties of such an anisotropic material. For this purpose, we propose to perform first-principles calculation to generate the reflectance of SrNbO$_{3.4}$, as this quantity is easily understood to interpret the characteristic of any materials. By considering its reflectance curve along each crystal direction, one would expect to know how this material responds to the external electromagnetic radiation and understand the meaning of anisotropic property of the crystal itself.

2. Computational method

Since reflectance depends on the real and imaginary parts of complex dielectric function, we need to calculate those spectra before going beyond. We use Density Functional Theory (DFT) [10, 11] implemented in Quantum ESPRESSO package [12] to get the complex dielectric function within independent particle level. An important thing to note in this calculation is that the complex dielectric function, especially the imaginary part one, is sensitive to the number of k-points sampling [13–15]. Therefore, we do the convergence study first before generating the reflectance spectra. We use the $N \times N \times 3 \Gamma$-centered Monkhorst-Pack k-points meshes and take $N = 12, 18, 24, 30$ in each calculation.

For DFT calculation, we implement the Optimized Norm-Conserving Vanderbilt Pseudopotential (ONCV) [16] from Schlipf-Gygi norm-conserving pseudopotential library [17]. Those pseudopotentials treat Sr-4s$^4$p$^5$s, Nb-4s$^4$p$^5$s$^4$d, and O-2s$^2$p as valence states. The cut-off kinetic energy of the wavefunctions is set to 50 Ry while cut-off kinetic energy of charge density and potential is set to the default value. The atomic position of perovskite ($n = 5$) SrNbO$_{3.4}$ is taken from ref. [18], as in figure 1, and the Fermi level is adjusted by using variable `tot_charge` in order to get the same result as the experiment [7, 8, 19]. We use `tot_charge` = 0.72 as this value leads to a minimum criterion to capture the anisotropic characteristic of this material.

Because of the anisotropic property of the material, we cannot consider the optical response function only along a certain direction. We must also investigate the complex dielectric function along other crystal axes and then conclude which k-points grid yields the converged spectra. We then generate the reflectance spectra after having the optimum k-points grid in hand.
3. Results and discussion

The results of convergence study are summarized in figure 2a to figure 2c. One important thing is that these spectrum are plotted from $\omega = 0.025$ eV instead since the resulting data are not well-defined at $\omega = 0$ eV. By considering these results, one can notice that along $a$ crystal axis it has the Drude peak which indicates the metallic behavior, while along the other directions this characteristic does not appear. This remarkable result yields the conclusion that this material has a highly anisotropic property. Focusing attention on the convergence study of $\varepsilon_2$, the converged spectra is obtained by using $N = 18$ k-points grid for $\varepsilon_2$ along $b$ and $c$ crystal axes. However, this value is surprisingly different if one considers the $\varepsilon_2$ along $a$ crystal axis.

Along this direction, there are several discrepancies as the effect of varying k-points sampling. First to note is the peak around 0.4 eV. Under $N = 12$, this peak is still split into two peaks. By increasing the number of k-points sampling, one can achieve the converged spectra by using $N = 18$. The second to note is the peak around 1.0 eV. Increasing the number of k-points sampling leads to the red-shifted peak even after using $N = 30$. This trend suggests us to not using the smaller number of k-points, and by carefully inspecting the peak position under k-points grid variations one can regard whether $N = 24$ or $N = 30$ as the converged spectra. The third thing to consider is the Drude peak. Because the limited range of data, one cannot actually investigate the Drude peak position. However, the position can be

![Figure 2](image-url)

**Figure 2.** Optical response functions of SrNbO$_{3.4}$. Panels (a) to (c) show the results of convergence study of complex dielectric function along each crystal axis with respect to the number of k-points sampling. Panel (d) shows the resulting reflectance spectra of the material under optimum k-points grid.
regarded as the extrapolation of the well-defined data in the spectra. From this point of view, it can be noticed that there is an anomaly as the number of k-points increases. At $N = 24$, the peak position reaches the highest value while at $N = 30$ the peak position decreases. It means that we must consider higher number of k-points in the convergence study, but it is not possible since we are limited by our computing resources. Hence, we must choose between $N = 24$ or $N = 30$ which yields the better spectra. From physical point of view, calculation within DFT is done at independent particle level and therefore one should encounter the independent particle characteristic in its dielectric function. The $N = 24$ spectra shows a good agreement with that because it displays the similar crossing behavior with y axis of the graph, unlike the $N = 30$ spectra which exhibits the very rare behavior to be called as the Drude peak. By this argument, and concluding the overall discussion of convergence study, one can state that in order to get the converged spectra, the $N = 24$ is the trustworthy value physically and numerically.

By using the results of the convergence study described above, the reflectance spectra is generated as in figure 2d. This optical quantity ensures the anisotropic property of this material, that it perfectly reflects the photon which has the frequency below the plasma frequency ($\omega_p \approx 1.0$ eV) along the $a$ crystal direction and poorly reflects the photon on the other directions. In other words, we have the material which is metal and insulator at the same time which depends on what direction we consider. Nevertheless, this calculation still lacks corrections. As stated earlier, the DFT calculates the complex dielectric function independent of particle level and therefore we do not include the effect of electron-electron and electron-hole interactions yet. However, as a first study, this reflectance spectra is a good reference to interpret the physical property of highly anisotropic material.

4. Conclusion
In conclusion, we have presented a DFT study to calculate the dielectric functions and the reflectance of SrNbO$_{3.4}$ as a representative of a highly anisotropic material. The converged spectra of complex dielectric function which is sensitive to the number of k-points sampling is achieved after using the $24 \times 24 \times 3$ Monkhorst-Pack k-points meshes. This choice is obtained not only by considering the numerical cost, but also the physical meaning behind it. This number of k-points sampling yields the reflectance spectra which becomes the strong evident that the SrNbO$_{3.4}$ material has a highly anisotropic property. Despite the meaningful results obtained in this study, we acknowledge that our results are subject to some corrections as we have not yet included either electron-electron or electron-hole interactions in this study.

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