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First-principles study on the optical properties of $KNbO_3$

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Abstract
We report our studies on the electronic structure and linear and nonlinear optical (NLO) properties of $KNbO_3$ using a first-principles method in the local density approximation (LDA). The calculated results for the refractive indices and second-harmonic-generation (SHG) coefficients agree well with experimental results. From decomposing the nonlinear susceptibility, we find that the primary contribution to the NLO behaviour comes from the hybridization of the O 2p and Nb 4d electron states. In addition, there are two different roles played by the O atoms because of their different distances from the Nb atom; thus we propose a possible way to enhance the SHG coefficients.

Potassium niobate ($KNbO_3$) is a well-known ferroelectric material. Extensive theoretical and experimental studies have been carried out ever since the discovery of the ferroelectricity in this compound [1]. However, most of the theoretical works mainly concentrated on the ferroelectricity and/or structural instability [2–6]. To the best of our knowledge, theoretical studies on the optical properties of this material are almost nonexistent. In fact, $KNbO_3$ is a very interesting NLO material: e.g., it shows frequency doubling in the near-IR range and excellent photorefractive properties, which can be further enhanced by doping with Fe atoms [7], to the extent that Fe:$KNbO_3$ is considered as a material that might potentially be developed for high-capacity optical memory applications. Therefore, in order to understand these above-stated optical properties, a theoretical investigation is necessary to study first the electronic structure, then the optical properties of a pure $KNbO_3$ crystal.

In this work, we report results of a theoretical calculation of the electronic and optical properties of $KNbO_3$ using the *ab initio* self-consistent linearized augmented-plane-wave (LAPW) method with the von Barth–Hedin exchange–correlation term [8, 9]. In particular, we report calculations of the SHG coefficients and discuss the mechanism of the SHG processes. Recently, the same approach was applied successfully to another kind of complex NLO material, i.e., borate crystals [10, 11].

At ambient temperature, $KNbO_3$ is ferroelectric and belongs to the orthorhombic space group $Amm2$ with ten atoms ($Z = 2$) in the unit cell. We begin our band theory calculation by using the experimental structure [12]. The muffin-tin radii of K, Nb and O are set equal to 1.40, 1.05 and 0.83 Å, respectively. Thirty six special $\boldsymbol{k}$-points in the irreducible wedge of the Brillouin zone (BZ) are used in the self-consistent iterations. About 700 LAPW basis functions are used at each $\boldsymbol{k}$ point. The convergence, measured by the rms difference between the input and output charge density, is 0.005 me au^{-3}.

In figure 1, we show the calculated total and partial densities of states of $KNbO_3$. As we can see, the bottom of the conduction band is mostly derived from Nb 4d electron states. While the O 2p electrons dominate the top of the valence band, a mixture of Nb 4d and O 2p electron states in the valence band (-5 to 0 eV) is also significant. K electron states locate in the upper part of the conduction band (>8 eV) and the lower part of the valence band (<-10 eV). This band structure is very similar to that of $BaTiO_3$ [13], which displays the same succession of phase transitions as $KNbO_3$. The calculated energy gap for $KNbO_3$ is 2.2 eV at Γ, which is smaller than the experimental value[1] 3.1 eV, a typical finding in a LDA calculation.

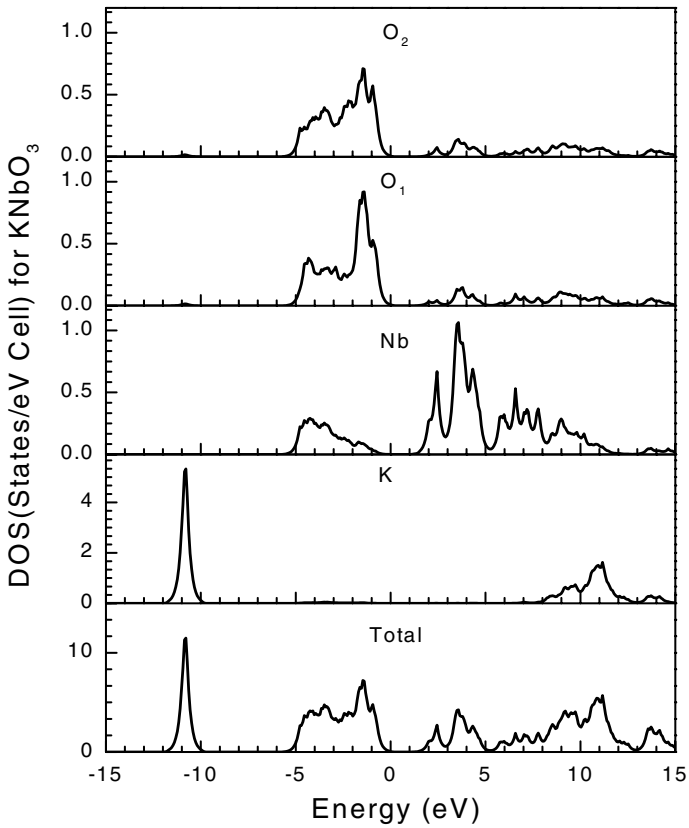

Figure 1. Calculated total and partial densities of states of $KNbO_3$.

We now carry out the theoretical study on the optical properties of this material. Calculation of the linear and nonlinear optical properties using the LAPW method has been discussed in detail elsewhere [10, 11]; thus we focus on presenting our results here.

[1] Calculated from the absorption edge, 0.4 μm.

The linear optical properties of $KNbO_3$ are investigated using 36 special $\boldsymbol{k}$-points in the irreducible BZ. The calculated dielectric constant (averaged over the three Cartesian directions) $\varepsilon = 6.04$ exceeds the experimental value 4.69 [6]. Since $KNbO_3$ is a negative biaxial crystal, three refractive indices are listed in table 1 together with corresponding experimental values [14]. The calculated anisotropic orders of the refractive indices agree well with experimental results.

Table 1. Calculated refractive indices of $KNbO_3$.

	n_X	n_Y	n_Z
Theory	2.54	2.46	2.36
Experiment ($\lambda = 3.0\ \mu$m)	2.18	2.15	2.06

It is well known that failing to precisely predict the band gap in the LDA framework may jeopardize the calculation of the optical properties. In the past, many authors adopted a relatively simple method named 'scissors correction' to overcome this LDA problem [15–18]. However, we find that even a rather sophisticated form of this correction [19] could not improve our present results. This may suggest that the energy shift should be $\boldsymbol{k}$-dependent to achieve a better result for $KNbO_3$, which makes the calculation complicated. Recently, calculations beyond LDA approaches, e.g., the application of the generalized gradient approximation (GGA) and nonlocal density functionals [20], have been proven to improve upon LDA results for a wide range of problems. This looks to be a promising approach for handling the optical properties of ferroelectric materials. However, as an initial step and in order to avoid complexity, our present results are given only in a plain LDA form; no further correction is made.

The calculated linear absorption spectra with three different polarization directions of $KNbO_3$ are shown in figure 2. The absorption edge starts from about 2.2 eV, corresponding to the energy gap. This originates from a transition from the O 2p electron states located at

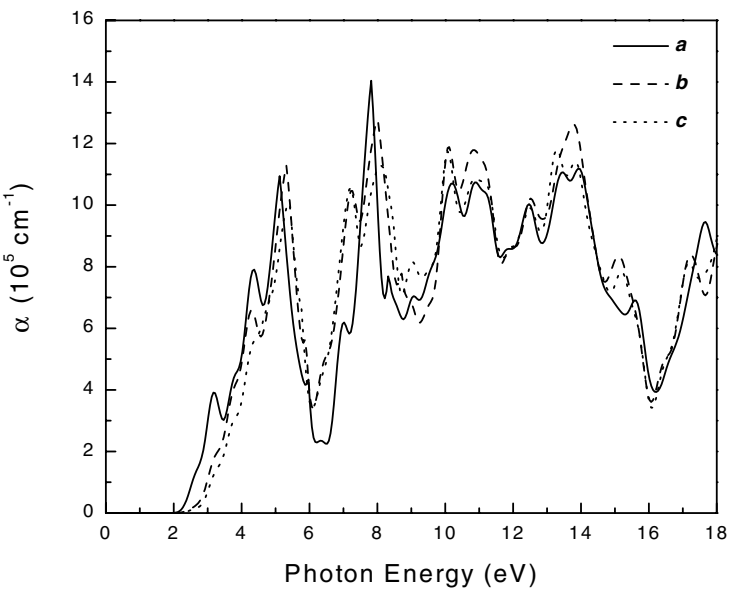

Figure 2. Linear absorption coefficients of $KNbO_3$. Labels a, b and c represent the polarization directions of the photon along the crystal axes a, b and c, respectively.

the top of the valence bands to the empty Nb 4d electron states dominating the bottom of the conduction bands. After several small but noticeable shoulders, the curve reaches its first peak at about 5.2 eV. This value is approximately the distance between the two largest peaks of the upper valence bands and the lower conduction bands shown in figure 1. Thus we can see that Nb and O atoms play very important roles in the optical properties of $KNbO_3$. At the same time, we notice that the K atom makes almost no contribution to the low-energy part of the linear absorption spectra; this is because its electron states are not in the domain of major interest. In addition, we observe that the linear absorption is anisotropic along different crystal axes, but the main features of these curves are almost the same.

We also calculate three independent SHG components, i.e., d_{31} $(=\frac{1}{2}\chi^{(2)}_{311})$, d_{32} $(=\frac{1}{2}\chi^{(2)}_{322})$ and d_{33} $(=\frac{1}{2}\chi^{(2)}_{333})$. We find that a large number of special $\boldsymbol{k}$-points should be included to compute the nonlinear optical properties of $KNbO_3$. But for practical reasons, we use 80 $\boldsymbol{k}$-points in the irreducible BZ in our calculation. The discrepancies between these results and those obtained by using 175 $\boldsymbol{k}$-points are within 5%. The calculated results and the experimental values for these independent SHG components are listed in table 2. As can be seen from the table, our results give the correct magnitude and relative sign of these components; in particular, the calculated value for d_{31} is very close to the experimental one. In view of the complexity both in the experimental determination and the theoretical calculation of the SHG coefficients, the agreement is better than expected.

Table 2. SHG coefficients of $KNbO_3$ ($d_{31} = \frac{1}{2}\chi^{(2)}_{311}$, $d_{32} = \frac{1}{2}\chi^{(2)}_{322}$, $d_{33} = \frac{1}{2}\chi^{(2)}_{333}$) in units of 10^{-9} esu.

	Plain LDA	Experiment
d_{31}	28.2	27.5[a]
d_{32}	−65.3	−31.5[a]
		−48.9[b]
d_{33}	−25.2	−48.0[a]

[a] Reference [21].
[b] Reference [22].

In order to understand the nature of the nonlinear process, we apply the same decomposition technique as was used in reference [11]. In brief, we calculate the spectral and spatial decompositions of $\chi^{(2)}$, which reveal the contributions from each constituent of the unit cell and their electron states. Here we choose $\chi_{333}(0)$ as an example. In figure 3, we present the decompositions with respect to the initial valence band energy of different types of atom. We can see that O and Nb atoms contribute primarily to the major feature of the curve in the panel labelled 'Total'. Similarly to the linear case, Nb–O hybridization is also a dominant factor in the NLO response of $KNbO_3$.

We also notice that the roles of the two different types of O atom are quite different. The O2 atom makes a significant negative contribution to $\chi_{333}(0)$ (notice that this coefficient has a negative value), while the O1 atom makes almost no negative contribution. This is rather surprising, since their densities of states are very similar (figure 1). As we know, the room temperature phase of $KNbO_3$ is a perovskite structure distorted along its [110] direction. Considering a Nb–O octahedron, this distortion makes four O atoms (O2) change their distances from the centre Nb atom (from 2.00 to 1.87 Å), while the other two O atoms (O1) remain almost unchanged. Therefore this distortion breaks the inversion symmetry, and separates the O atoms into two types; thus their different interactions with Nb atom are what make the SHG processes possible.

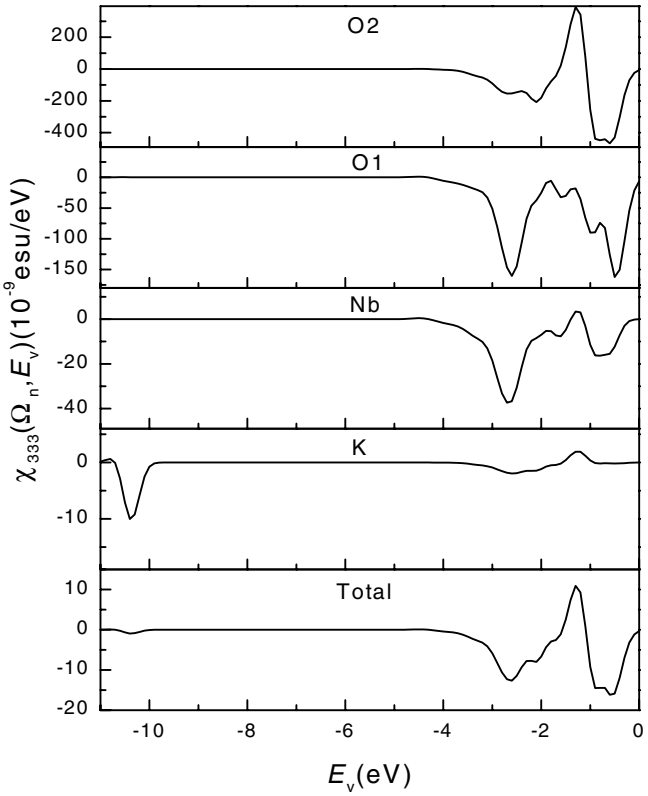

Figure 3. $\chi^{(2)}_{333}(0)$; spectral and spatial decomposition with respect to the initial valence band energy of $KNbO_3$.

On the basis of these observations, we find that it is possible to enhance the SHG coefficients of $KNbO_3$ by slightly shifting the positions of O2 atoms. Experimentally, this corresponds to a lattice strain along the original cubic [110] direction. This change is so small that we expect it not to affect the O1 atom much. As for the O2 atom, this change may decrease its negative contribution to the SHG components. As a result, it may enhance the SHG coefficients.

In practice, we decrease the Wyckoff positions of the O2 z-coordinates by 0.01. This operation maintains the $Amm2$ group symmetry but changes the nearest Nb–O2 distance from 1.87 to 1.91 Å. Then $\chi_{333}(0)$ changes to -115.3×10^{-9} esu, which is about double the original value. In figure 4, we show the change of the role played by O2 atom. As we see, O2 atoms make a significant contribution to the SHG coefficient χ_{333}, which causes this profound change.

Finally it should be pointed out that although we mainly discuss the Nb–O bonding here, the importance of the K cation cannot be ignored. As indicated by Cohen [13], the A cation in an ABO_3 compound has an effect on the B–O bonding interaction. Thus the K atom may have an indirect effect on the optical properties of $KNbO_3$.

In summary, we have studied the electronic structure and linear and nonlinear optical properties of $KNbO_3$ by means of a first-principles calculation. The calculated results are in good agreement with experiments in a LDA framework. Our research reveals that the Nb–O bonding interaction is very important to the optical properties of the room temperature phase of $KNbO_3$. We also find that the contributions of two inequivalent O atoms are different in the

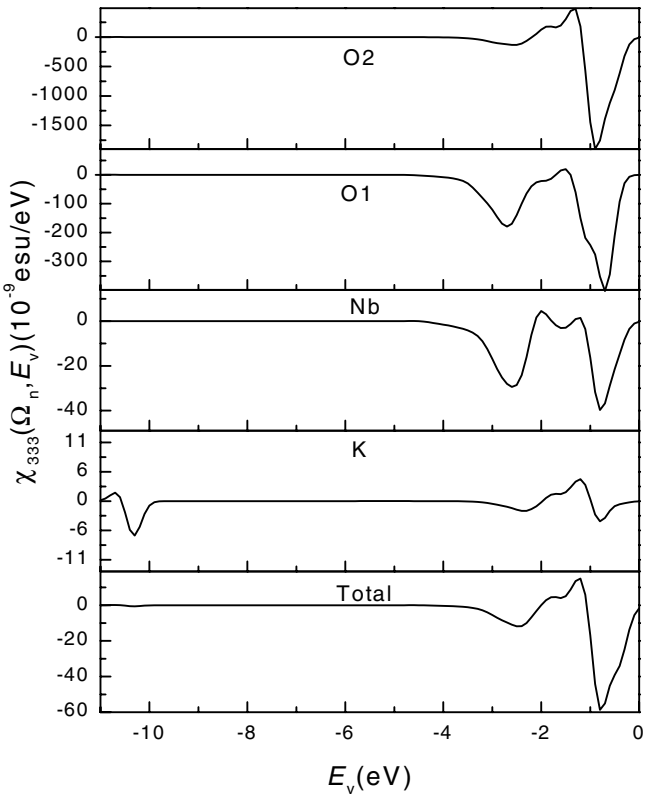

Figure 4. As figure 3, except that the results are obtained from shifting the positions of O2 atoms.

SHG process. On the basis of this finding, we propose a way to enhance the value of the SHG coefficients of a material like $KNbO_3$, by varying the positions of certain atoms, e.g., applying static pressure in a certain direction.

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