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Abstract. Second-order non-linear optical tensor coefficients of $LiNbO_3$-type compounds have been obtained on the basis of crystallographic data and a bond-orbital model, which is capable of calculating single bond contributions to the second-order non-linear optical susceptibility. The tensor values thus calculated are in good agreement with experimental data. The influence of energy-band broadening on the non-linear optical susceptibility is not well accounted for in the bond-orbital model.

1. Introduction

Non-linear optical (NLO) materials are important materials for device applications. To understand more about NLO materials in order to improve their properties, a number of theoretical models that calculate the quantitative NLO response of crystalline compounds have been derived.

Bergman and Crane [1], for instance, have determined the second-order NLO bond polarizabilities $\beta^{\parallel}$ and $\beta^{\perp}$ for various types of chemical bond by relating the NLO bond polarizabilities to the experimental tensor coefficients d_{ij} of NLO materials by means of three-dimensional geometrical factors (G_{ij} and G'_{ij}). The summation is taken over all the chemical bonds m in the unit cell volume V.

$$d_{ij} = \frac{1}{V} \sum_m (G_{ij}\beta^{\parallel} + G'_{ij}\beta^{\perp}_m). \tag{1}$$

With these β values [1] the NLO tensor coefficients of new NLO materials can be calculated via (1).

It is evident that the NLO bond polarizabilities $\beta^{\parallel}$ and $\beta^{\perp}$ depend strongly on the bond length. However, the bond parameter model of Bergman and Crane uses only mean values of $\beta^{\parallel}$ and $\beta^{\perp}$, i.e. β values that correspond to a mean bond length, to describe the second-order NLO polarizabilities of each chemical bond.

To improve the bond-parameter model Jeggo and Boyd [2] tried to deduce a reliable expression for the bond-length dependence of $\beta^{\parallel}$ for several niobates and tantalates, but the results were not very satisfying. In these calculations $\beta^{\perp}$ was neglected, since its contribution to the NLO tensor coefficient is usually rather small [2].

After the bond-parameter model, other models were developed to describe the NLO response by means of a few well defined physical parameters. Kurtz [3], for instance,

showed that the MO_6 octahedra in ferroelectric compounds built up from oxygen octahedra play a key role in determining the optical properties of these materials. A simple relation was derived for the second-order NLO tensor coefficients and the energy of the lowest optical interband transitions, which take place between the O 2p and the metal (M) 3d, 4d or 5d orbitals depending on the M ion.

DiDomenico and Wemple [4] related the NLO response of ferroelectrics with O octahedra to the energy-band structure. A mean oscillator energy and an average oscillator strength were derived from a single-term Sellmeier description of optical refractive-index data, and related to the NLO tensor coefficients. Uchida [5] extended this single-oscillator model to a two-oscillator model by including the interband transition, which is commonly observed in ferroelectrics with O octahedra at an energy of 9–11 eV, to be compared with the lowest interband transition at 4–6 eV. It was shown that in the long-wavelength limit the 9–11 eV transition contributes more to the linear refractive index than the 4–6 eV transition.

Levine [6] derived an expression for the second-order NLO bond susceptibility of ABO_3 compounds, taking into account the bond length, the mean energy gap, and the difference in electronegativity of the bonding atoms. However, for calculation purposes too many unknown parameters are present in this expression.

Only recently Lines [7–9], inspired by the work of Harrison [10], derived a relation for the second-order NLO bond susceptibility $\chi_b^{(2)}$, which makes it possible to calculate $\chi_b^{(2)}$ from readily available parameters, such as the bond length and the energy-band structure as derived from (UV) reflectance spectra.

In this paper the above-mentioned model of Lines [7–9] is used to calculate the $\chi_b^{(2)}$ values of various covalent transition-metal–O bonds of different bond lengths. These $\chi_b^{(2)}$ values are used to calculate the second-order NLO tensor coefficients of several NLO materials via (1). The d_{ij} values thus obtained are discussed in relation to experimental data and d_{ij} values obtained via (1) with the mean β values derived by Bergman and Crane [1].

2. Theory

Let us first take a closer look at the bond-orbital model as derived by Lines [7–9]. In this model the non-linear electronic response is described as a perturbation of bonding orbitals by an applied electric field. The virtual electronic interband transitions, which dominate this response, take place between filled valence-band levels and empty conduction-band sp and d levels. The mean oscillator energies of these transitions are denoted as $E_{Sell,sp}$ and $E_{Sell,d}$, i.e. the Sellmeier energy for the sp and d transitions, respectively. Values of E_{Sell} are usually obtained from a fit of the linear refractive index n, or the linear dielectric constant ε, as a function of the wavelength [5, 11]. For ferroelectrics with O octahedra, such as the $LiNbO_3$-related compounds, the two interband transition energies discussed by Uchida [5] are ascribed by us to $E_{Sell,sp}$ and $E_{Sell,d}$.

If the bond length decreases, the d levels will decrease in energy and fall below the conduction sp band. Lines describes the bond-length dependence of $\chi_b^{(2)}$ as an influence of the empty cationic d orbitals on the NLO bond polarizability. This d-orbital contribution dominates the NLO response for bond lengths $\leqslant 2.0$ Å, whereas for bond lengths $\geqslant 2.3$ Å the sp-orbital contribution becomes important.

For covalent bonds the following expression for the sp-orbital (χ_{sp}) and d-orbital (χ_d) contributions is derived from [8] using $\alpha_i = S_i \sqrt{2}$ and $V_{2,i} = (E_{Sell,i} S_i)/2$:

$$\chi_i = -3\sqrt{2}(f_i)^2 e^3 S_i^2 (d + g_i \Delta)^2 (g_i d - \Delta S_i^2/a_i^2)/\{(E_{Sell,i})^2 a_i^2\} \qquad \text{with } i = \text{sp, d.} \qquad (2)$$

Here e is the electronic charge, f_i the orbital shielding factor, S_i the overlap integral, d the bond length (in metres), $\Delta = d\{(d/2R_M)^{1/2} - 1\}$ (in metres), R_M the cationic radius (in metres), $a_i^2 = 1 - S_i^2$, and $g_i = \{(1 - 2S_i^2)/2(1 - S_i^2)\}^{1/2}$.

The second-order NLO bond susceptibility is a summation of the two contributions χ_d and χ_{sp}

$$\chi_b^{(2)} = (\chi_{sp} + \chi_d)/4\pi\varepsilon_0. \tag{3}$$

Here the second-order NLO bond susceptibility $\chi_b^{(2)}$ is expressed in SI units, i.e. $m^4\ V^{-1}$.

Following (1) the second-order NLO bond susceptibility $\chi_b^{(2)}$ is related to d_{ij} (see the appendix)

$$d_{ij} = \frac{1}{V}\frac{1}{2}(f_L)^4 \sum_m G_{ij}\chi_{b,m}^{(2)} \tag{4}$$

with $f_L = ((n_\infty)^2 + 2)/3$. Here f_L is the Lorentz local-field enhancement factor [7–9] and n_∞ the long-wavelength refractive index.

By combining (1) and (4) it is found that

$$\beta_m^\| = \tfrac{1}{2}(f_L)^4\chi_{b,m}^{(2)}. \tag{5}$$

3. Results

3.1. Bond-orbital model

To check whether the bond-orbital model of Lines [7–9] gives reliable results, the second-order NLO bond susceptibility $\chi_b^{(2)}$ was calculated via (2) and (3) as a function of the bond length for Nb–O and W–O bonds (details of the parameters used in these calculations are discussed below). The results of these calculations are given in figure 1.

The curves in figure 1 show that the absolute values of $\chi_b^{(2)}$ increase with the bond length. This can be understood as follows. As the bond length increases, the bonding electrons will have less interaction with the nuclei, so that they will become more polarizable.

Furthermore, $\beta^\|$ values derived from these $\chi_b^{(2)}$ values via (5) are of the same order of magnitude as those derived by Bergman and Crane [1]. For instance, for an Nb–O bond with a bond length of 2.0×10^{-10} m a $\beta^\|$ of 46×10^{-40} $m^4\ V^{-1}$ is calculated (see also figure 1), whereas Bergman and Crane [1] derived an average value of $(52 \pm 4) \times 10^{-40}$ $m^4\ V^{-1}$ for Nb–O bonds.

From figure 1 it is also clear that the calculated $\chi_b^{(2)}$ values of the W–O bonds are about a factor of 2.5 larger than those of the Nb–O bonds. This agrees nicely with earlier results obtained from powder second-harmonic-generation (SHG) measurements on $Li_{1-x}Nb_{1-x}W_xO_3$ compounds (with $0 \leqslant x \leqslant 0.50$) [13].

So the bond-orbital model seems to be a rather reliable method to calculate NLO bond-susceptibility $\chi_b^{(2)}$ values. In the next sections the results of the calculations of the second-order NLO tensor coefficients of several NLO materials will be presented using the bond-orbital model to calculate NLO single-bond contributions.
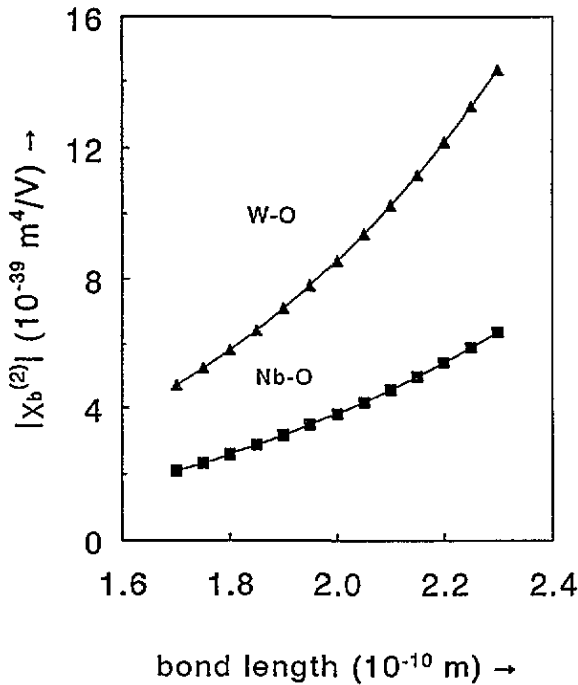
Figure 1. The absolute second-order NLO bond susceptibility as a function of the bond length.

Table 1. Some measured d_{ij} values.

Composition	d_{31}^a (pm V^{-1})	d_{33}^a (pm V^{-1})	Reference
$Li_{0.94}Nb_{1.01}O_3^b$	−5.3	−42.3	[12]
$Li_{0.96}Nb_{1.008}O_3^b$	−7.3	−45.6	[12]
$LiNbO_3$		−55 ± 14^c	This work
β-$LiNbWO_6$		−91 ± 23^c	[13]^d
$LiTaO_3$	−1.3 ± 0.2	−20.7 ± 2.5	[14]

^{a} The following conversion units are used: $d_{11}(SiO)_2 = 0.50$ pm V^{-1}; $d_{36}(KH_2PO_4) = 0.63$ pm V^{-1} [14].

^{b} The composition of the Li-deficient $LiNbO_3$ crystals was calculated on the basis of the work of Bordui et al [16], correlating T_c values to crystal compositions.

^{c} Effective tensor coefficients estimate from SHG measurements on stoichiometric $LiNbO_3$ powder.

^{d} In [13] the relative NLO response×$d_{33}(LiNbO_3)$ (in pm V^{-1}) is used, i.e. $d_{eff} = $ (relative NLO response)$^{1/2}d_{33}(LiNbO_3)$ (in pm V^{-1}) [14].

3.2. LiNbO$_3$-type compounds

In table 1 some measured second-order NLO tensor coefficients (d_{ij}) of several $LiNbO_3$-type compounds are given. The d_{ij} values in table 2 were calculated by relating either the NLO bond polarizabilities $\beta^{\parallel}$ and $\beta^{\perp}$ or the NLO bond susceptibility $\chi_b^{(2)}$ to d_{ij} via geometrical factors (see (1) and (4)).

In the first case, mean values of the NLO bond polarizabilities $\beta^{\parallel}$ and $\beta^{\perp}$ are used for each transition-metal–O bond. Absolute mean β values were derived from [1], with

Table 2. Some calculated $|d_{ij}|$ values.

Composition	Calculated according to Bergman and Crane [1]		Calculated according to bond-orbital theory [7–9]	
	$|d_{31}|$ (pm V^{-1})	$|d_{33}|$ (pm V^{-1})	$|d_{31}|$ (pm V^{-1})	$|d_{33}|$ (pm V^{-1})
Li$_{0.94}$Nb$_{1.01}$O$_3$	7.1	48.8	4.3	43.3
Li$_{0.96}$Nb$_{1.008}$O$_3$	7.7	52.0	4.5	46.2
LiNbO$_3$	9.0	59.3	5.1	52.8
β-LiNbWO$_6$	a	a	7.5	76.1
LiTaO$_3$	2.7	28.2	2.1	23.4

[a] No average β values for W–O bonds are available from the literature [1].

d_{36}(KH$_2$PO$_4$) $= 0.63$ pm V^{-1} [14]. It must be stressed that these β values have been calculated from experimentally known d_{ij} values via (1) by Bergman and Crane [1].

The other calculations were carried out with NLO bond-susceptibility $\chi_b^{(2)}$ values obtained from bond-orbital calculations [7–9]. The perpendicular component of the second-order NLO bond susceptibility is neglected in these calculations, i.e. $\chi_b^{(2)}(\perp) = 0$. In both cases only the more polarizable transition-metal–O bonds are considered [2]. In the bond-orbital model the contributions of other bonds amount to about 1% only.

The orbital shielding factors for the sp- and d-dominated energy levels used in (3) were obtained from [9]. For sp-orbital contributions $f_{sp} = (1.3 \pm 0.1)$, whereas for d-orbital contributions $f_d = (1.9 \pm 0.1)$. Appropriate S_i values were derived from [9] by scaling with $(1\sqrt{f_i})$. For the cationic radii R_M the values of Shannon and Prewitt [15] were used. For n_∞ a value of 2.15 was taken.

For the Sellmeier energies of the sp and d transitions the following values were used:

Nb–O	sp	8.5 eV	[11]	d	5.0 eV	[11]
W–O	sp	7.0 eV	[9]	d	3.4 eV	[13]
Ta–O	sp	7.0 eV	[9]	d	6.6 eV	[9].

3.3. Other NLO material

In table 3 the measured NLO tensor coefficients d_{31} and d_{33} of other important NLO materials, for instance, KTiOPO$_4$, are given. In table 4 the calculated values of the NLO tensor coefficients d_{31} and d_{33} are shown. These d_{ij} values were obtained in a similar way to those in table 2. Some details of the parameters used in these calculations can be found in the previous paragraph.

Table 3. Some measured tensor values of important NLO materials.

Composition	d_{33}^a (pm V^{-1})	d_{33}^a (pm V^{-1})	Reference
KNbO$_3$	-12.88 ± 1.03	-19.58 ± 1.03	[14]
Ba$_{0.5}$Sr$_{0.5}$Nb$_2$O$_6$	6.7 ± 2.1	17.7 ± 5.2	[14]
Ba$_{4.13}$Na$_{1.74}$Nb$_{10}$O$_{30}$	-20.0 ± 2.0	-27.5 ± 2.0	[14]
K$_{5.70}$Li$_{4.07}$Nb$_{10.23}$O$_{30}$	9.7 ± 1.3	17.5 ± 1.6	[14]
BaTiO$_3$	-23.4 ± 1.8	-8.8 ± 0.5	[14]
KTiOPO$_4$	10.0	21.1	[14]

[a] The following conversion units are used: d_{11}(SiO$_2$) $= 0.50$ pm V^{-1}; d_{36}(KH$_2$PO$_4$) $= 0.63$ pm V^{-1} [14].

Table 4. Some calculated $|d_{ij}|$ values of important NLO materials.

Composition	Calculated according to Bergman and Crane [1]		Calculated according to bond-orbital theory [7–9]	
	$|d_{31}|$ (pm V^{-1})	$|d_{33}|$ (pm V^{-1})	$|d_{31}|$ (pm V^{-1})	$|d_{33}|$ (pm V^{-1})
KNbO$_3$	14.1	28.6	9.9	32.3
Ba$_{0.5}$Sr$_{0.5}$Nb$_2$O$_6$	4.1	4.8	2.6	12.1
Ba$_{4.13}$Na$_{1.74}$Nb$_{10}$O$_{30}$	13.2	15.3	8.6	31.7
K$_{5.70}$Li$_{4.07}$Nb$_{10.23}$O$_{30}$	10.4	11.1	7.1	21.8
BaTiO$_3$	40.1	19.9	12.2	9.5
KTiOPO$_4$	2.6[a]	36.7[a]	5.1	18.1

[a] The NLO P–O bond contributions are also considered in these calculations [1].

For the Sellmeier energies of the sp and d transitions of the titanate compounds the following values were used:

$$\text{sp } 10.0 \text{ eV [9]} \qquad \text{d } 4.6 \text{ eV [9].}$$

4. Discussion

The advantage of the bond-orbital model over the method of Bergman and Crane is evident: it is possible to calculate the second-order NLO bond susceptibility for every chemical bond from readily available parameters, whereas Bergman and Crane could only determine the second-order NLO bond polarizabilities for a limited number of chemical bonds [1].

A comparison between the measured d_{ij} values in table 1 and the calculated d_{ij} values in table 2 shows that the bond-orbital model gives more accurate results than the method of Bergman and Crane [1]. So on the whole the bond-orbital model seems to be a good method to estimate the d_{ij} values of LiNbO$_3$-type compounds.

The large NLO response of β-LiNbWO$_6$ is ascribed to the more polarizable W–O bonds. W–O bonds have $\chi_b^{(2)}$ values about 2.5 times larger than those of Nb–O bonds (see also figure 1). The difference in NLO bond susceptibility is largely due to a difference in $E_{\text{Sell,d}}$ values, which is in agreement with earlier findings [13].

This brings us to the most crucial point of this work, i.e. the general application of the bond-orbital model. When using the bond-orbital model in combination with appropriate bond parameters (see also (3)) to estimate the d_{ij} coefficients of other NLO materials, for instance KNbO$_3$ or KTiOPO$_4$, relatively large deviations of up to about 50% were found (see table 3 and 4 for details).

With the method of Bergman and Crane [1] even larger differences between the calculated and measured d_{ij} values were found (see tables 3 and 4). This is ascribed to the fact that the bond-length dependence of β was neglected, whereas the influence of energy-band broadening on the second-order NLO polarizabilities $\beta^{\parallel}$ and $\beta^{\perp}$ was not considered at all by Bergman and Crane [1].

The reason that the bond-orbital model gives poor results may lie in some of the assumptions made in this model. Important NLO materials, for instance KNbO$_3$ and KTiOPO$_4$, have a delocalized excited state. In LiNbO$_3$-type compounds, however, the energy-band broadening is considerably less [17, 18]. In LiNbO$_3$, for instance, the width of the 4d conduction band is about 2.3 eV [18]. This width is for the greater part due to

the crystal-field splitting of the d orbitals. The actual band broadening of a single d level is ~ 1 eV.

Unfortunately, the electronic band structure of $KNbO_3$ has not been calculated. However, when going from $LiNbO_3/LiTaO_3$ to $KNbO_3/KTaO_3$ the spectral differences between the alkali niobates and tantalates become smaller. This has been ascribed to an increase in the amount of electronic delocalization [17]. Therefore, we compared the band structure of $LiNbO_3$ with that of $KTaO_3$. In $KTaO_3$ [19] the width of the total 5d conduction band is about 7 eV, whereas the crystal-field splitting is about 3 eV. In $SrTiO_3$ [19] (3d band) the situation is about the same. This implies that according to calculations the broadening of energy levels in $KTaO_3$ is of more importance than that in $LiNbO_3$. The difference is about a factor of three. This agrees with the conclusions we obtained from optical spectroscopy before [17].

The calculated d_{ij} values of the $LiNbO_3$ compounds are in agreement with the experimental data, whereas for $KNbO_3$ and other NLO materials with a delocalized excited state the calculated NLO tensor values differ by up to about 50% from the experimental data.

In the bond-orbital model, energy-band broadening is thought to be largely accounted for by a change in the mean oscillator energies $E_{\text{Sell,sp}}$ and $E_{\text{Sell,d}}$. The present results suggest that the influence of the electronic delocalization on the NLO properties cannot simply be described by a change in the mean oscillator energies (see also (3)). Apparently, the influence of energy-band broadening on the energy-band structure is rather complicated.

From previous work [20] it was already known that the NLO response of NLO materials increases as the amount of electronic delocalization increases. A theoretical study of the NLO properties of $KTiOPO_4$, taking into account the influence of–Ti–O–Ti–O–chains, supports this view: the non-resonant hyperpolarizability is shown to be enhanced if more TiO_6 units are added into the calculation [21]. However, it is difficult to derive a relation between the NLO response and the amount of electronic delocalization.

Another more obvious reason for the difference between the calculated and experimental d_{ij} values may be the following. In the bond-orbital model and the second-order non-linear optical bond susceptibility perpendicular to the bond axis is neglected, although Bergman and Crane [1] have shown that 'experimental' $\beta^{\perp}$ values of transition-metal–O bonds can amount to about 15% of the $\beta^{\parallel}$ values. Because this neglect does not seem to play an important role in the case of the $LiNbO_3$-type compounds, this cannot explain the differences found here.

In conclusion, the present method, which calculates second-order NLO tensor coefficients d_{ij} from crystallographic data and second-order NLO bond susceptibilities $\chi_b^{(2)}$, which are obtained with a bond-orbital model, works satisfactorily for $LiNbO_3$-type compounds, i.e. for NLO materials with a low amount of electronic delocalization.

Appendix

The second-order NLO bond susceptibility is related to χ_{ij}, the macroscopic second-order NLO susceptibility, as follows [8]:

$$\chi_{ij} = \frac{1}{V} \sum_m G_{ij} \chi_{b,m}^{(2)} f_L \qquad \text{(A1)}$$

with $f_L = ((n_\infty)^2 + 2)/3$. The macroscopic susceptibility χ_{ij} is related to d_{ij} in the following way [22]:

$$d_{ij} = \tfrac{1}{2}(f_L)^3 \chi_{ij}. \qquad \text{(A2)}$$

The factor of one-half arises from the difference between the experimental and theoretical representations of time-varying electromagnetic fields [14].

Combining (A1) and (A2), d_{ij} is related to $\chi_{b,m}^{(2)}$ as

$$d_{ij} = \frac{1}{V}\frac{1}{2}(f_L)^4 \sum_m G_{ij}\chi_{b,m}^{(2)}. \tag{A3}$$

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