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Non-linear optical susceptibilities and electro-optic tensor of some ferroelectrics: first principle study

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The linear and nonlinear optical properties of some ferroelectrics ($BaTiO_3$, $KNbO_3$, $LiTaO_3$ and $LiNbO_3$) are studied by density functional theory (DFT) in the local density approximation (LDA) expressions based on first principle calculations without the scissor approximation. Specially, we present calculations of the frequency- dependent complex dielectric function $\varepsilon(\omega)$ and the second harmonic generation response coefficient $\chi^{(2)}$ (-2ω,ω,ω) over a large frequency range in tetragonal and rhombohedral phases. The electronic linear electrooptic susceptibility $\chi^{(2)}$ (-ω,ω,0) is also evaluated below the band gap. These results are based on a series of the LDA calculation using DFT. Results for $\chi^{(2)}$ (-ω,ω,0) are in agreement with experiment below band gap and those for $\chi^{(2)}$(-2ω,ω,ω) are compared with experimental data where available.

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1. Introduction

Nowadays, nonlinear optics has developed a field of major study because of rapid advance in photonics [1]. Nonlinear optical techniques have been applied to many diverse disciplines such as condensed matter physics, medicine and chemical dynamics. The development of new advanced nonlinear optical materials for special applications is a crucial importance in technical areas such as optical signal processing and computing, acousto-optic devices and artificial neuro-network implementation. There are intense efforts in experimenting, fabricating and searching for various nonlinear optical materials including ferroelectrics and related compounds. However there is comparatively a much smaller effort to understand the nonlinear optical process in this materials at the microscopic level. Theoretical understanding of the factor that control the figure of merit is extremely important in improving the existing electrooptic (EO) materials and in the search for new ones[2].

Even though there exist a number of calculations for the electronic band structure and optical properties using different methods [3-10]. There is a large variation in the energy gaps, suggesting that the energy band gap depends on the method of the energy spectra calculation. We therefore thought it worthwhile to perform calculations using density functional theory (DFT) in the local density approximation (LDA) expressions, as implemented within ABINIT package[8] the following convention. Static fields will be labeled by Greek indices (α,β,…) while we refer to optical fields with Latin symbols (i,j,…). To simplify the notation, we will also drop labels such as ∞ for quantities that do not involve the response of the ions. Using this convention, we can write ε_{ij} and $\varepsilon_{\alpha\beta}$, respectively, for the optical and static dielectric tensors, respectively, and $r_{ij\gamma}$ for the linear EO tensor that involves two optical and one static electric fields.

In this paper, we describe details calculations of the linear and nonlinear optical properties, includes linear electro-optic tensor for some ABO_3 ferroelectrics (A= Ba, K, Li, B=Ti, Ta, Nb) with oxygen octahedral structure. Our calculations will highlight the effect of replacing Ti by Nb and Nb by Ta (and also replacing Ba by Li and Li by K) on the optical properties in ABO_3 ferroelectrics. Our aim in this study is to understand the origin of the $\chi^2(\omega)$ and r_{ijk} in these materials as well as to study the trends with moving from Ti to Nb and Nb to Ta (Ba→Li→K).

Our paper is organized as follows. In sec.2, we describe the methodology, structure and computational details. In sec.3, we describe the computation of the nonlinear optical susceptibilities and linear EO tensor. In sec.4, we illustrate the validity of the formalism by applying methodology and theory (see sec.2 and sec.3) to ABO_3 ferroelectrics. Some of the tensor we consider in this work depends on static electric fields: They include contributions of both the electrons and the ions. Other quantities imply only the response of the valence electrons: They are defined for the frequencies of the electric fields high enough to get rid of the ionic contributions but sufficiently low to avoid electronic excitations. For clarity, we adopt.

2. Computational details

The nonlinear optical properties of ABO_3 were theoretically studied by means of first principles calculations in the framework of density functional theory (DFT) and based on the local density approximation

(LDA)[11] as implemented in the ABINIT code[8,12]. The self–consistent norm-conserving pseudopotentials are generated using Troullier-Martins scheme [13] which is included in the Perdew-Wang [14] scheme as parameterized by Ceperly and Alder [15]. For calculations, the wave functions were expanded in plane waves up to a kinetic-energy cutoff of 40 Ha ($LiNbO_3$ and $LiTaO_3$), 35 Ha (tetragonal and rhombohedra $KNbO_3$), 38 Ha ($BaTiO_3$). The Brillouin zone was sampled using a 6 x 6 x 6 the Monkhorst-Pack[16] mesh of special k points. Rhombohedral position coordinates of $LiNbO_3$ and $LiTaO_3$ using both experimental value [17,18] were calculated to relate to the hexagonal coordinates given in the literature by the transformation[19]. The coordinates of $KNbO_3$ [20] and $BaTiO_3$[21] are reported in Table 1. All calculation of ABO_3 has been used with the experimental lattice constants and atomic positions. The lattice constants and atomic positions are given in Table 1. The coordinates of the other atoms can easily be obtained by using the symmetry operations of the space groups. These parameters were necessary to obtain converged results in the nonlinear optical properties and phonons data at Γ point of the Brillouin zone.

Table 1. The lattice parameters and atomic positions in ABO_3.

Phase	Space Group	Lattice Parameters (Å)	Atom	Position
$LiNbO_3$ Ferroelectric (Rhombohedral)	R3c	a = b = c = 5.4944	Li Nb O	(0.2829, 0.2829, 0.2829) (0.0, 0.0, 0.0) (0.1139,0.3601,-0.2799)
$LiTaO_3$ Ferroelectric (Rhombohedral)	R3c	a = b = c = 5.4740	Li Ta O	(0.2790, 0.2790, 0.2790) (0.0, 0.0, 0.0) (0.1188,0.3622, -0.2749)
$KNbO_3$ Ferroelectric (Tetragonal)	P4mm	a = b = 3.9970 c = 4.0630	K Nb O(1) O(2)	(0.0, 0.0, 0.023) (0.5, 0.5, 0. 5) (0.5, 0.5, 0.04) (0.5, 0.0, 0.542)
$KNbO_3$ Ferroelectric (Rhombohedral)	R3m	a = b = c = 4.0160	K Nb O(1) O(2)	(0.0112,0.0112, 0.0112) (0.5, 0.5, 0. 5) (0.5295,0.5295, 0.0308) (0.5295,0.0308, 0.5295)
$BaTiO_3$ Ferroelectric (Tetragonal)	P4mm	a = b = 3.9909 c = 4.0352	Ba Ti O(1) O(2)	(0.0, 0.0, 0.0) (0.5, 0.5, 0.5224) (0.5, 0.5, -0.0244) (0.5, 0.0, 0.4895)

3. Linear and nonlinear optical response

3.1 Linear optical response

It is well known that the effect of the electric field vector, $E(\omega)$, of the incoming light is to polarize the material. In an insulator the polarization can be expressed as a Taylor expansion of the $E(\omega)$

$$P^i(\omega)=P_s^i+\sum_{j=1}^{3}\chi_{ij}^1(-\omega,\omega)E^j(\omega)+\sum_{j,l=1}^{3}\chi_{ijl}^2E^j(\omega)E^l(\omega)+\ldots \quad (1)$$

where P_s^i is the zero field (spontaneous) polarization, χ_{ij}^1 is the linear optical susceptibility tensor and is given by ref. [22].

$$\chi_{ij}^1(-\omega,\omega)=\frac{e^2}{\hbar\omega}\sum_{n,m,\vec{K}}f_{nm}(\vec{K})\frac{r_{nm}^i(\vec{K})r_{mn}^j(\vec{K})}{\omega_{mn}(\vec{K})-\omega}=\frac{\varepsilon_{ij}(\omega)-\delta_{ij}}{4\pi} \quad (2)$$

where n, m denote energy bands, $f_{mn}(\vec{K})=f_m(\vec{K})-f_n(\vec{K})$ is the Fermi occupation factor, and Ω is the normalization volume. $\omega_{mn}(\vec{K})\equiv[\omega_m(\vec{K})-\omega_n(\vec{K})]$ is the frequency difference and $\hbar\omega_n(\vec{K})$ is the energy of band n at wave vector $\vec{K}$. The $\vec{r}_{nm}$ are the matrix elements of the position operator and are given by

$$r_{nm}^i(\vec{K})=\frac{v_{nm}^i(\vec{K})}{i\omega_{nm}};\omega_n\neq\omega_m \quad (3)$$

$$r_{nm}^i(\vec{K})=0,\omega_n=\omega_m$$

where $v^{i}_{nm}(\vec{K}) = [P^{i}_{nm}(\vec{K})/m]$, m is the free electron mass, and P_{nm} is the momentum matrix element. χ^{2}_{ijl} the second-order nonlinear susceptibility tensor and will discusses in sec.4. As can be seen from Eq.2, the dielectric function $\varepsilon_{ij}(\omega) = [1 + 4\pi\chi^{1}_{ij}(-\omega,\omega)]$ and the imaginary part of $\varepsilon_{ij}(\omega)$, $\varepsilon^{ij}_{2}(\omega)$ is given by

$$\varepsilon^{ij}_{2}(\omega) = \frac{e^{2}}{\hbar\pi}\sum_{nm}\int d\vec{K} f_{nm}(\vec{K}) \frac{v^{j}_{nm}(\vec{K}) v^{j}_{mn}(K)}{\omega^{2}_{mn}} \delta(\omega - \omega_{mn}(K)) \quad (4)$$

The real part of $\varepsilon_{ij}(\omega), \varepsilon^{ij}_{1}(\omega)$, can be obtained by using Kramers-Kronig transformation

$$\varepsilon^{ij}_{1}(\omega) - 1 = \frac{2}{\pi} \mathrm{P}\int_{0}^{\infty} \frac{\omega' \varepsilon^{ij}_{2}(\omega')}{\omega'^{2} - \omega^{2}} d\omega' \quad (5)$$

As the Kohn-Sham equations only determine the ground-state properties, hence the unoccupied conduction bands have no physical significance. If they are used as single-particle states in optical calculation of semiconductors, a band gap problem comes into existence: The absorption starts at a too low energy [23]. In order to remove the deficiency the many-body effects must be included in calculations of response functions. In order to take into account the self-energy effects., generally used the scissors approximation [23]. In the calculation of the optical response in present work we have used the standard expression for $\varepsilon_{ij}(\omega)$ (see Eq.4 and 5).

3.2 Nonlinear response

The general expression of the nonlinear optical susceptibility depends on the frequencies of the $E(\omega)$. Therefore, in present context of the (2n+1) theorem applied within the LDA to DFT we get expression for the second order susceptibility[22-25]. As the sum of the three physically different contributions

$$\chi^{2}_{ijl}(-\omega_{\beta}-\omega_{\gamma},\omega_{\beta},\omega_{\gamma}) = \chi''_{ijl}(-\omega_{\beta}-\omega_{\gamma};\omega_{\beta},\omega_{\gamma}) + \eta''_{ijl}(-\omega_{\beta}-\omega_{\gamma},\omega_{\beta},\omega_{\gamma}) + i\frac{\sigma''_{ijl}(-\omega_{\beta}-\omega_{\gamma},\omega_{\beta},\omega_{\gamma})}{\omega_{\beta}+\omega_{\gamma}} \quad (6)$$

That includes contributions of interband and intraband transitions to the second order susceptibility. The first term in Eq.6 describes contribution of interband transitions to second order susceptibility. The second term represents the contribution of intraband transitions to second order susceptibility and the third term is the modulation of interband terms by intrabands terms. We have used this expression to calculate nonlinear response functions of ABO_3 ferroelectrics.

3.3 Principal refractive indices calculation

The principal refractive indices, n_i, can be computed as a square root of the eigenvalues of the optical dielectric tensor. At finite temperature, T, we can write $< \varepsilon_{ij}(u_r,\eta) >= \delta_{ij} + 4\pi < \mu^{1}_{ij}(u_r,\eta) >$ where <···> refers to the average value at a given T. Let us write u_r and η as $u_r =< u > + \delta u_r$ and $\eta =< \eta > + \delta\eta$, where δu_r and $\delta\eta$ denote the deviations from average values (here, u_r - the ionic degree of freedom in r unit cell, η - the macroscopic strains). If we develop $< \chi^{1}_{ij}(u_r,\eta) >$ as a Taylor expansion about the paraelectric structure, we can separate the terms depending on $< u >$ and $< \eta >$ only from those involving also δu_r and $\delta\eta$. At finite temperature, the dielectric susceptibility can therefore be expressed as

$$< \chi^{1}_{ij}(u_r,\eta) >= \chi^{1}_{ij}(< u >,< \eta >) + < \chi^{1}_{ij}(< u >,< \eta >,\delta u_r,\delta\eta) > \quad (7)$$

The first term describes the variations of χ^{1}_{ij} due to the averaged crystal lattice distortions. It is responsible for the discontinuity of n_i at the phase transition in ferroelectrics such as $BaTiO_3$. The second term represents the variations of χ^{1}_{ij} due to thermal fluctuations and to their correlations [2]. It determines the variations of n_i in the paraelectric phase. This term is difficult to compute in practice. However, in usual ferroelectric such as $BaTiO_3$ or $KNbO_3$, the variations of n_i in the paraelectric phase are small compared to their variation at the phase transition. Following ref.[22] we will neglect the second term in Eq.7 since we are interested in the variation of n_i below the phase transition temperature (T_c) where we expect the first term to dominate. The linear EO effect is related to the first order change of the optical dielectric tensor induced by a static or low frequency electric field (E).

3.4 Electro-Optic tensor

The optical properties of material usually depend on external parameters such as the temperature, electric or magnetic fields or mechanical constraints (stress, strain). Now we consider the variations of the refractive index induced by a static or low-frequency electric field E. At linear order, these variations are described by the linear electro-optical (EO) coefficients (Pockels effect).

$$\Delta(\varepsilon^{-1})_{ij} = \sum_{k=1}^{3} r_{ijk} E_k \quad (8)$$

where $(\varepsilon^{-1})_{ij}$ is the inverse of the electronic dielectric tensor and r_{ijk} the EO tensor. Within the Born-Oppenheimer approximation, the EO tensor can be expressed as the sum of the three contributions: a bare electronic part r^{el}_{ijk} an ionic contribution r^{ion}_{ijk} and a piezoelectric contribution r^{piezo}_{ijk}. The electronic part is due to an interaction of E_k with the valence electrons when considering the ions artificially as clamped at their equilibrium positions. It can be computed from the nonlinear optical coefficients. As can be seen from Eq.6 χ^{2}_{ijl} defines the second order change of the induced polarization with respect to E_k. Taking the derivation of Eq.8 we also see that χ^{2}_{ijl} defines the first-order change of the linear dielectric susceptibility, which is equal to $(1/4\pi)\Delta\varepsilon_{ij}$. Since the EO tensor depends on $\Delta(\varepsilon^{-1})_{ij}$ rather than $\Delta\varepsilon_{ij}$, we have to transform $\Delta\varepsilon_{ij}$ to $\Delta(\varepsilon^{-1})_{ij}$ by the inverse of the zero-field electronic dielectric tensor [34].

$$\Delta(\varepsilon^{-1})_{ij} = -\sum_{m,n=1}^{3} \varepsilon^{-1}_{im}\Delta\varepsilon_{mn}\varepsilon^{-1}_{nj} \tag{9}$$

Using Eq.9 we obtain the following expression for the electronic EO tensor:

$$r^{el}_{ijk} = -8\pi \sum_{l,l'=1}^{3} (\varepsilon^{-1})_{il}\chi^{2}_{ll'k}(\varepsilon^{-1})_{l'j} \tag{10}$$

Eq.10 takes a simpler from when expressed in the principal axes of the crystal under investigation [34]:

$$r^{el}_{ijk} = -\frac{8\pi}{n_i^2 n_j^2}\chi^{2}_{ijk} \tag{11}$$

where n_i coefficients are the principal refractive indices.

The origin of ionic contribution to the EO tensor is the relaxation of the atomic positions due to the applied electric field E_k and the variations of the ε_{ij} induced by these displacements. It can be computed from the Born effective charge $Z^{*}_{k,\alpha,\beta}$ and the $\partial\chi_{ij}/\partial T_{k\alpha}$ coefficients introduced in [34]. The ionic EO tensor can be computed as a sum over the transverse optic phonon modes at $\vec{q} = 0$.

$$r^{ion}_{ijk} = -\frac{4\pi}{\sqrt{\Omega} n_i^2 n_j^2}\sum_{m}\frac{\alpha^{m}_{ij}P_{mk}}{\omega_m^2} \tag{12}$$

where α^{m} is the Raman susceptibility of mode m and $P_{m,k}$ the mode polarity

$$P_{mk} = \sum_{k',\beta} Z^{*}_{k',k\beta}u_m(k'\beta) \tag{13}$$

which is directly linked to the make oscillator strength

$$S_{m,\alpha\beta} = P_{m,\alpha}P_{m\beta} \tag{14}$$

For simplicity, we have expressed Eq.14 in the principal axes while a more general expression can be derived from Eq.10.

Finally, the piezoelectric contribution is due to a relaxation of the unit cell shape due to the converse piezoelectric effect [34]. It can be computed from the elasto-optic coefficients $P_{ij\mu\nu}$ and the piezoelectric strain coefficients $d_{k\mu\nu}$:

$$r^{piezo}_{ijk} = \sum_{\mu,\nu=1}^{3} P_{ij\mu\nu}d_{k\mu\nu} \tag{15}$$

In the discussion of the EO effect, we have to specify whether we are dealing with strain-free (clamped) or stress-free (unclamped) mechanical boundary conditions. The clamped EO tensor r^{η}_{ijk} takes into account the electronic and ionic contributions but neglects any modification of the unit cell shape due to the converse piezoelectric effect [7].

$$r^{\eta}_{ijk} = r^{el}_{ijk} + r^{ion}_{ijk} \tag{16}$$

Experimentally, it can be measured for frequencies of E_k high enough to eliminate the relaxations of the crystal lattice but low enough to avoid excitations of optical phonon modes (usually above ~ 10^2 MHz). To compute the unclamped EO tensor r^{σ}_{ijk} we have added the piezoelectric contribution to r^{η}_{ijk}. In the noncenterosymmetric phases of ABO_3 the EO tensor has four independent elements r_{13}, r_{33}, r_{22}, $r_{15} = r_{42}$. In contrast to the dielectric tensor, the EO coefficients can either be positive or negative. The sign of these coefficients is often difficult to measure experimentally. Moreover, it depends on the choice of the Cartesian axes. The z axes is along the direction of the spontaneous polarization and the y – axis lies in a mirror plane. The z and y –axes are both piezoelectric. Their positive ends are chosen in the direction that becomes negative under compression. The orientation of these axes can easily be found from pure geometrical arguments. Our results are reported in the Cartesian axes where the piezoelectric coefficients d_{22} and d_{33} are positive. These coefficients, as well as their total and electronic part, are reported in Table 2. All EO coefficients are positive as is the case for the noncentro-symmetric phases [7], the phonon modes that have the strongest overlap with the soft mode of the paraelectric phase dominate the amplitude to the EO coefficients. Moreover, the electronic contributions are found to be quite small. All our investigation of EO coefficients of ABO_3 shows a good agreement and also between our results and earlier investigations.

Table 2. EO tensors of some ABO_3 crystals.

Crystals	Symmetry Class	EO coefficients x 10^{-7} (esu)			
			Electronic	Total	Exp.
$BaTiO_3$	4mm	r_{13}	0.358	1.653	3.06 [27]
		r_{33}	0.505	3.570	12.18 [27]
$KNbO_3$	4mm	r_{13}	0.288	1.279	
		r_{33}	1.029	5.117	
		$r_{51} = r_{42}$	0.288	1.279	
	3m	r_{13}	0.569	3.417	
		r_{33}	0.942	6.276	
		$r_{51} = r_{42}$	0.623	3.459	
		r_{22}	0.254	1.333	
$LiNbO_3$	3c	r_{13}	0.230	1.756	2.58 [28]
		r_{33}	0.082	6.085	9.24 [28]
		$r_{51} = r_{42}$	0.236	1.879	8.40 [28]
		r_{22}	0.002	0.402	1.02 [28]
$LiTaO_3$	3c	r_{13}	0.092	3.513	2.52 [29]
		r_{33}	0.718	5.151	0.06 [29]
		$r_{51} = r_{42}$	0.091	1.105	9.15 [29]
		r_{22}	0.039	0.132	-6.00 [29]

4. Results and discussion

The calculation of nonlinear optical properties is much more complicated than the same procedure in the linear case. The difficulties concern both the numerical and the physics. The k-space integration in expression (6) has to be performed more carefully using a generalization of methods [24-26]. More conduction bands have to be taken into account to reach the same accuracy. The fact that the SHG coefficients are related to the optical transitions has remarkable consequences. First of all, we note that the equations for SHG consist of a number of resonant terms. In this sense the imaginary part, $\mathrm{Im}\chi^{(2)}(-2\omega,\omega,\omega)$ resembles the $\epsilon_2(\omega)$ and provides a link to the band structure. The difference, however, is that whereas in $\epsilon_2(\omega)$ only the absolute value of the matrix elements squared enters, the matrix elements entering the various terms in $\chi^{(2)}$ are more varied. They are in general complex and can have any sign. Thus, $\mathrm{Im}\chi^{(2)}(-2\omega,\omega,\omega)$ can be both positive and negative. Secondly, there appear both resonances when 2ω equals a interband energy and when ω equals an interband energy. Fig. (1-5) shows the 2ω and single ω resonances contributions to $\mathrm{Im}\chi^{(2)}(-2\omega,\omega,\omega)$ compared to $\epsilon_2(\omega)$ (Fig. 6) for a number of ABO_3. They clearly show a greater variation from high symmetry to lowest symmetry than the linear optic function. In some sense they resemble a modulated spectrum. Third, we note that the 2ω resonances occur at half the frequency corresponding to the interband transition. Thus, the incoming light need not be as high in the UV to detect this higher lying interband transition. This is important for wide band gap materials like ABO_3 compounds where laser light sources reaching the higher interband transitions are not available. Nevertheless, one still needs to be able to detect the corresponding 2ω signal in the UV. Unfortunately the intrinsic richness of $\chi^{(2)}$ spectra remains largely to be explored experimentally we are not aware of any attempts to measure both the real and imaginary parts of the these spectral functions as one standard does in linear optics. Also, it is well known that nonlinear optical properties are so sensitive to small changes in the band structure than the linear optical properties. That is attributed to the fact that the second harmonic response $\chi^{(2)}_{ijk}(\omega)$ contains 2ω resonance along with the usual ω resonance. Both the ω and resonances can be further separated into inter-band and intraband contributions. The structure in $\chi^{(2)}_{ijk}(\omega)$ can be understood from the structures in $\epsilon_2(\omega)$. Our calculations for $\epsilon_2(\omega)$ give two fundamental oscillator bands at ~6 and ~10 eV which correspond to the optical transitions from the valance bands to the conduction band, formed by the d orbits of the B (Ti,Nb,Ta) atoms and consisting of two subbonds. It is well known that the $\epsilon_2(\omega)$ function computed from moments ($\vec{p}$) appear to be very sensitive to the ab initio parameters and seem to be particularly appropriate to test electronic band structure. In ABO_3 perovskites the two peak present in experimental reflectivity data are obtained in theoretical curves only when the interband transition moments varied with respect to the energies and $\vec{k}$ wave vectors. In this computation on ABO_3, compounds many parameters have been barrowed from existing computations have been neglected, explaining some discrepancies between theory and experiments [9-10, 30-35]. The structure 2-6 eV in $\chi^{(2)}_{ijk}(\omega)$ is associated with interference between a ω and 2ω resonances, while the structure above 6 eV is due to mainly to ω resonance. In Fig. 1-5 we show the 2ω interband and intraband contributions for ABO_3 compounds. Also given is their decomposition into intra- and interband contributions. They are arranged so as to move the Ba → K → Li, Ti → Nb → Ta trends obvious. For example $\chi^{(2)}$ obviously increases when going from Ba to K and Li and from Ti to Nb. Unfortunately, the agreement between theory and experiment is by no means perfect [36].

Note that the interband part are negative in all cases and in most cases largely compensate the intraband part. The exceptions are the $LiBO_3$ (B=Nb,Ta) compounds in both cases of which interband part is much smaller in magnitude than the intraband part. This quite interesting because unexpected. It raises the question what features in the band structure of these two compounds distinguish them from the other compounds[37,38]. Recently, in ref.[39] were computed A_i (i=1,2) and E phonon modes and nonlinear optical susceptibilities for $LiNbO_3$. Knowledge of these modes can be relevant for further theoretical EO studies. We investigated the reasons for the cancellation of intra- and interband parts by inspecting the corresponding frequency dependent imaginary parts of the $\chi^{(2)}$ (-2ω,ω,ω). First of all, one now sees that the opposite sign of intra- and interband parts not only occurs in the static value but occurs almost energy by energy. This is true over the entire energy range in $BaTiO_3$ and over most of the range (E >1 eV) for other ABO_3. The sign of the inter and intraband part are difficult to understand *a- priori* because a variety of matrix element products comes into play and both ω and 2ω resonances occur in both the pure interband, and the interband contribution modified by intraband motion when these are further worked out into separate resonance terms. The spectra $\epsilon_2(\omega)$ (Fig. 6) for the ABO_3 compounds are rather similar. They look like the superposition of the spectra of more or less four pronounced oscillators with resonance frequencies close to the M and Z line structures appearing in the 2ω and ω – terms of the imaginary parts.

As an example of such a prediction the SHG coefficients of ABO_3 compounds are given in Table 3. For incident light with a frequency small compared to the energy gap. The independent tensor components are listed for ω=0. the comparison with recent experimental values and theoretical calculations[40] are also rather successful where available for the static SHG coefficients of the ABO_3 compounds.

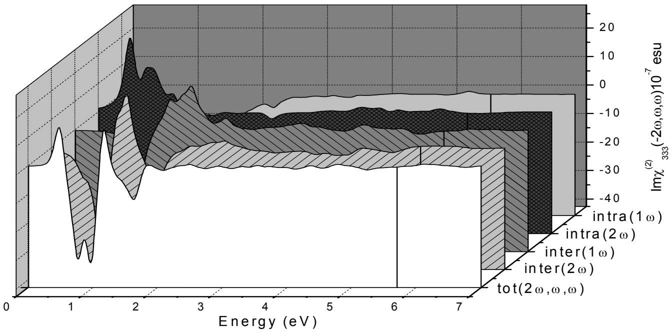

Fig. 1. Second-order susceptibility Im χ^{2}_{333} *(-2ω,ω,ω) for* $BaTiO_3$

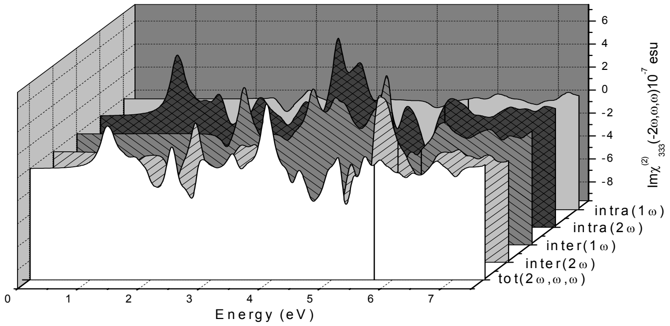

Fig. 2. Second-order susceptibility Im χ^{2}_{333} *(-2ω,ω,ω) for tetragonal* $KNbO_3$*.*

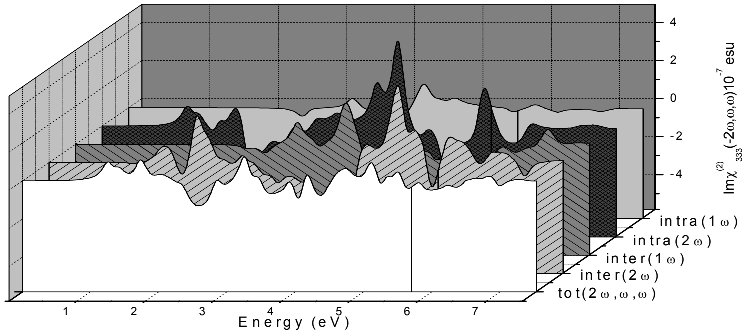

Fig. 3. Second-order susceptibility Im χ^{2}_{333} (-2ω,ω,ω) for rhombohedral KNbO$_3$.

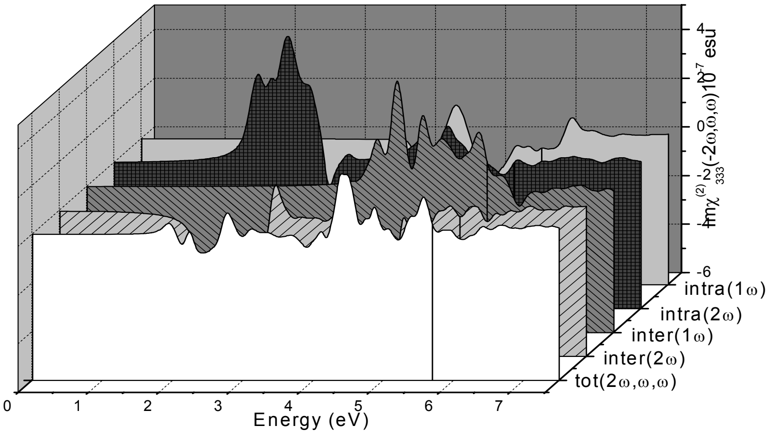

Fig. 4. Second-order susceptibility Im χ^{2}_{333} (-2ω,ω,ω) for LiNbO$_3$

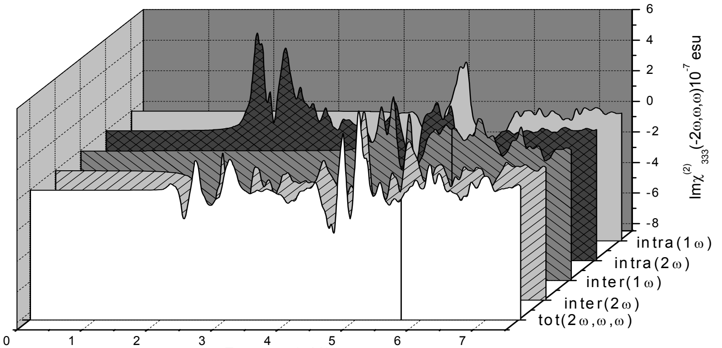

Fig. 5. Second-order susceptibility Im χ^{2}_{333} (-2ω,ω,ω) for LiTaO$_3$

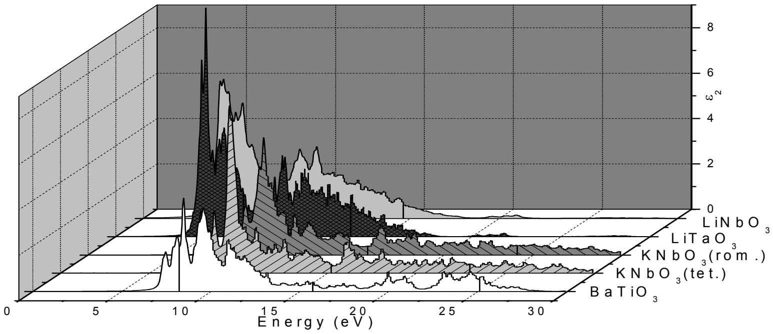

Fig. 6. The calculated imaginary part of z –components of the dielectric function of ABO_3.

Table 3. Second-order nonlinear optical susceptibilities for some ABO_3 crystals.

Crystals	Symmetry Class		d_{il} x 10^{-7} (esu)				
			d_{15}	d_{22}	d_{31}	d_{33}	Ref.
$BaTiO_3$	4mm	(cal.)	2.547	-	2.547	2.885	
		(exp)	5.1	-	4.71	2.040	[40]
$KNbO_3$	4mm	(cal.)	2.190	-	2.190	5.322	
		(cal.)	-	-	-0.299	-0.818	[40]
	3m	(cal.)	-	1.546	3.465	4.788	
		(cal.)	-	0.342	0.121	0.342	[40]
$LiNbO_3$	3c	(cal.)	-	0.013	1.541	6.877	
		(exp.)	-	0.774	-1.464	-10.2	[41]
$LiTaO_3$	3c	(cal.)	-	0.221	0.513	4.114	
		(exp.)	-	0.51	-0.321	-4.92.)	[41]

5. Conclusion

The linear and nonlinear optical properties for important group of oxygen-octahedron ferroelectrics ABO_3 ($LiNbO_3$, $LiTaO_3$, $KNbO_3$ and $BaTiO_3$) have been calculated over a wide energy range. We studied some possible combination of A and B. This allowed us to study the trends in the second order optical response with chemical composition. The results for the zero-frequency limit of second harmonic generation in agreement with available experimental results. The calculated linear electrooptical coefficients for $LiNbO_3$, $LiTaO_3$, $KNbO_3$ and $BaTiO_3$ are also show agreement with recent experimental data in the energy region below band gap. For all the considered compounds the SHG coefficient $\chi^{(2)}$ is of the order of ~10^{-7} esu. Our calculations of the SHG susceptibility shows that the intra-band and interband contributions are significantly changes with change B and A – ions.

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