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Calculation of third-order non-linear optical susceptibility of metal–oxide crystals

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Abstract. Third-order susceptibility tensor components of metal–oxide crystals are calculated using an approach based on the bond charge model used previously for the calculation of $\chi^{(2)}$ and $\chi^{(3)}$ of simple crystal structures. Calculated values of $\chi^{(3)}$ of $PbMoO_4$, $CaWO_4$, $CaCO_3$ and KDP are compared with the experimental data.

1. Introduction

The study of cubic susceptibility $\chi^{(3)}$ is very important because it is responsible for such non-linear effects as self-focusing, self-phase modulation, four-wave-mixing processes, Raman scattering and others. Third-order processes are expected to be a base for the construction of all optical switching devices [1].

The development of models to calculate $\chi^{(3)}$ gives rise to the possibility of predicting the values of the tensor components of non-linear susceptibilities in crystals not investigated experimentally. Moreover, the comparison of the theoretical and experimental results for $\chi^{(3)}$ helps to evaluate the correct models to describe susceptibilities in crystals.

There are several approaches for the calculation of non-linear optical susceptibilities. The most accurate model is the quantum mechanical approach [2]. It is only applied for the simplest crystals [3] because of the need for a lot of computer resources to calculate the accurate wavefunctions and energies for a large number of excited states.

The other models are based on approximations. The theory of bond orbitals [4] gives a simple method to approximately calculate the eigenstates of the crystals. Using the bond orbital model, Phillips [5] and Van Vechten [6] developed a dielectric description of ionicity that has been successfully employed in many areas connected with crystal structures. In particular they obtained the expression of $\chi^{(1)}$ for tetrahedral crystal structures. Levine [7, 8] extended this theory for other types of crystal structures and developed, on its basis, an electrodynamical model for $\chi^{(2)}$ that gives excellent agreement with experiments.

Chemla [9] developed further the $\chi^{(2)}$ theory of Levine and adapted it for the calculation of $\chi^{(3)}$ in semiconductor crystals with simple structure. The application of this model for other metal–oxide crystals does not give acceptable agreement with experiment. In particular this theory does not give the correct sign of $\chi^{(3)}$ in $PbMoO_4$.

To our knowledge, a model for calculation of $\chi^{(3)}$ in metal–oxide crystals with mixed ionic and covalent bonds has not been published. In this paper we present a model for calculation of the magnitude and sign of $\chi^{(3)}$ tensor components of metal–oxide crystals. The model is a modification of the Bond Charge Model (BCM) used previously by Levine [8] for calculation of $\chi^{(2)}$ and by Chemla [9] for calculation of $\chi^{(3)}$. The calculations are compared with the experimental data.

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2. Calculation method

The main idea in the model described above is the calculation of the microscopic cubic hyperpolarizability of the bonds in the crystal γ_{ijkl} and after that the summation over all bonds in the elementary cell.

Let α be the mean bond polarizability which is macroscopically defined by [5]:

$$\alpha = \tfrac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp}) = \frac{1}{4\pi N_{\mathrm{b}}} \frac{(h\Omega_{\mathrm{p}})^2}{E_{\mathrm{g}}^2}. \tag{1}$$

In this formula $\alpha_{\parallel}$ is the polarizability along the bond, $\alpha_{\perp}$, the polarizability in the perpendicular direction and N_{b}, the number of bonds per cm^3. The plasma frequency Ω_{p}, in this relation, is obtained from the number of valence electrons N_{e} using

$$(h\Omega_{\mathrm{p}})^2 = DA(4\pi N_{\mathrm{e}}\, \mathrm{e}^2/m_{\mathrm{e}}) \tag{2}$$

where D and A are correction factors with magnitudes close to one. E_{g} is the mean energy gap that according to Phillips [5] consists in two parts: homopolar E_{h} and heteropolar C and

$$E_{\mathrm{g}}^2 = E_{\mathrm{h}}^2 + C^2. \tag{3}$$

These two parts define the ionicity of the bond

$$f_{\mathrm{i}} = C^2/E_{\mathrm{g}}^2. \tag{4}$$

We have used the following definitions for E_{h} and C of the $\mathrm{A}_m\mathrm{B}_n$ bond [5]:

$$E_{\mathrm{h}} = 39.74 d^{-2.48} \tag{5}$$

$$C = b\,\mathrm{e}^{-kr_0}\left(\frac{Z_{\mathrm{a}}}{r_{\mathrm{a}}} - \frac{n}{m}\frac{Z_{\mathrm{b}}}{r_{\mathrm{b}}}\right). \tag{6}$$

Here d is the distance between atom A and atom B, r_{a} and r_{b} are the covalent radii (i.e. $d = r_{\mathrm{a}} + r_{\mathrm{b}}$) and Z_{a} and Z_{b} are the numbers of valence electrons. The term $b\,\mathrm{e}^{-kr_0}$, where $r_0 = d/2$, is the Thomas–Fermi screening factor in which b is a constant that is approximately 1.5 for most of the crystals under investigation.

We did not use the Levine expression for E_{h}^2 [8], which includes dependencies on r_{a} and r_{b}, because this expression is in agreement with Phillips theory only when $r_{\mathrm{a}} = r_{\mathrm{b}}$. For bonds with $r_{\mathrm{a}} \neq r_{\mathrm{b}}$ expression (5) gives values for the ionicity f_{i} that are much closer to the known experimental values. Moreover, using the Levine expression in our model we obtain an incorrect sign for $\chi^{(3)}$ for the $\mathrm{PbMoO_4}$ crystal.

Let us first find the non-linear solution for one bond. For this purpose we will suppose that the non-linearity is caused by the displacement of the bond charge q, which is localized between atom A and atom B, at distances r_{a} and r_{b} respectively, as a function of the applied electrical field E. Expanding α in powers of E we obtain:

$$\alpha_{ij}(E) = \alpha_{ij}(0) = \sum_k \beta_{ijk} E_k + \sum_{kl} \gamma_{ijkl} E_k E_l \tag{7}$$

where β and γ are the second- and third-order bond susceptibilities:

$$\beta_{ijk} = \left(\frac{\partial \alpha_{ij}}{\partial E_{kl}}\right)_{E=0} \qquad \gamma_{ijkl} = \left(\frac{\partial^2 \alpha_{ij}}{\partial E_k \partial E_l}\right)_{E_0}. \tag{8}$$

For the case when the electrical field E is directed along the bond, the induced moment is $\delta rq = \alpha_{\parallel} E_{\parallel}$ and the changes in r_{a} and r_{b} can be represented as:

$$\Delta r_{\mathrm{a}} = -\Delta r_{\mathrm{b}} = \delta r = \frac{\alpha_{\parallel} E_{\parallel}}{q} \tag{9}$$

where according to the BCM the bond charge is $q = (2/\varepsilon_\mathrm{h})e$ (ε_h is the homopolar part of dielectric constant ε, e is the electron charge unit).

For the field E perpendicular to the bond:

$$\Delta r_{\mathrm{a,b}} = \frac{\delta r^2}{2r_{\mathrm{a,b}}} = \frac{\alpha_\perp^2 E_\perp^2}{2r_{\mathrm{a,b}} q^2}. \tag{10}$$

The non-zero tensor components of the cubic bond polarizability of an axially symmetric bond are

$$\gamma_{zzzz} = \gamma_\parallel \qquad \gamma_{xxxx} = \gamma_{yyyy} = 3\gamma_{xxyy} = \gamma_\perp. \tag{11}$$

To find $\gamma_\parallel$ and $\gamma_\perp$ we use the fact that α is a function of charge displacement δr

$$\alpha(\delta r) = A_0 + A_1\delta r + A_2\delta r^2 + A_3\delta r^3 + \cdots. \tag{12}$$

The displacement δr can be defined from the expansion of the polarizability of one bond $p = \delta r q$ and it is:

$$\delta r = \frac{1}{q}(\alpha(0)E + \beta E^2 + \gamma E^3). \tag{13}$$

Substituting (13) in (12) we obtain:

$$\alpha(\delta r(E)) = A_0 + \frac{A_1\alpha(0)}{q}E + \left(\frac{A_1\beta}{q} + \frac{A_2\alpha^2(0)}{q^2}\right)E^2 + \cdots. \tag{14}$$

Comparing with (7) we obtain

$$\alpha(0) = A_0 \qquad \beta = \frac{A_1\alpha(0)}{q} \qquad \gamma = \frac{A_1^2\alpha(0) + A_2\alpha^2(0)}{q^2} \tag{15}$$

where

$$A_0 = \frac{1}{N_\mathrm{b}4\pi}\frac{(h\Omega_\mathrm{p})^2}{E_\mathrm{g}^2} \tag{16}$$

$$A_1 = \frac{\partial}{\partial\delta r}\left(\frac{1}{N_\mathrm{b}4\pi}\frac{(h\Omega_\mathrm{p})^2}{E_\mathrm{g}^2}\right)_{\delta r=0} \tag{17}$$

$$A_2 = \frac{\partial^2}{\partial(\delta r)^2}\left(\frac{1}{N_\mathrm{b}4\pi}\frac{(h\Omega_\mathrm{p})^2}{E_\mathrm{g}^2}\right)_{\delta r=0} \tag{18}$$

and must be calculated for both $E_\parallel$ and $E_\perp$.

Macro-susceptibility $\chi^{(3)}$ is obtained by summarization of the contributions of all the bonds in the crystal cell

$$\chi_{IJKL}^{(3)} = 4N_\mathrm{cell}\sum_s\sum_{ijkl}\cos(\theta_{Ii})\cos(\theta_{Jj})\cos(\theta_{Kk})\cos(\theta_{Ll})\gamma_{ijkl,s} \tag{19}$$

where N_cell is the number of elementary cells in 1 cm^3, θ_{Ii} is the angle between axis I of the co-ordinate system connected with the bond and axis i of the crystallographic co-ordinate system and s is an index that covers different bonds.

3. Calculation of $\chi^{(3)}$ of some metal–oxide crystals

We used this $\chi^{(3)}$ model for the calculation of the cubic non-linearity $\chi^{(3)}(-\omega, \omega, \omega, -\omega)$ for some crystals with sheelit structure, $CaCO_3$ and KDP. Calculations were done for a pump beam with $\lambda = 532$ nm. In this type of crystal, as our calculations show, the main contribution to $\chi^{(3)}$ is from oxide groups: MoO_4 group for $PbMoO_4$, WO_4 for $CaWO_4$, CO_3 for $CaCO_3$ and PO_4 for the KDP crystal. The calculated values for diagonal components of $\chi^{(3)}$ are compared with the experimental data in table 1. The agreement between the experimental and calculated data seems to be good for $PbMoO_4$ and $CaWO_4$ crystals. There are some difficulties with crystals with flat oxide groups, as in the case of $CaCO_3$. In this case there are electronic orbitals directed perpendicular to the plane of the flat group. This may explain the observed discrepancy between experimental and calculated values for $CaCO_3$. Further development of this model based on anionic group theory [12] is needed to take into account the contributions of these orbitals. At this point we have to note that, although the role of the cations is small, it should not be totally neglected.

Table 1. Comparison of the calculated and experimental data for $\chi^{(3)}$ of some metal–oxide dielectric crystals.

	Bond with predominant	Ionicity of the bond	Bond hyperpolarizability (10^{-37} esu)		$\|\chi^{(3)}\|$ Theoretical (10^{-14} esu)		$\|\chi^{(3)}\|$ Experimental (10^{-14} esu)			
Crystal	contribution	(%)	$\gamma_\parallel$	$\gamma_\perp$	$\chi^{(3)}_{xxxx}$	$\chi^{(3)}_{zzzz}$	$\chi^{(3)}_{xxxx}$	$\chi^{(3)}_{zzzz}$	error (%)	ref.
$PbMoO_4$	Mo–O	48	−72	−55	68	58	86	48	17	[10]
$CaWO_4$	W–O	49	−4.2	−0.78	1.8	1.7	2.1	2.8	15	[9]
$CaCO_3$	C–O	46	0.036	0.074	0.13	0.23	0.48	0.33	15	[9]
KDP	P–O	41	−0.62	−0.15	0.16	0.12	0.28	0.31	15	[9]

The calculated components are negative for $PbMoO_4$, $CaWO_4$ and KDP crystals and positive for the $CaCO_3$ crystal. In [11], using the phase-conjugate interferometric method, we measured the sign of the $\chi^{(3)}$ components of $PbMoO_4$ relative to the component $\chi^{(3)}_{xxxx}$ of CS_2, now accepted as a standard for positive cubic non-linearity. The negative sign measured for the $\chi^{(3)}_{xxxx}$ and $\chi^{(3)}_{zzzz}$ components is in agreement with our calculations. The method used in [10], for the measurement of the $\chi^{(3)}$ components in $CaWO_4$, $CaCO_3$ and KDP, does not allow sign determination.

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