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Structural Aspects of Nonlinear Optics—Oxide Systems ABO_x

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Nonlinear optical properties of several oxide systems ABO_x (A = Li, Na, Ba, etc.; B = Nb, Ti, I, etc.) will be discussed with respect to current microscopic theories. Recent calculations of microscopic bond (nonlinear) polarizabilities (β's) show that the conventional one-dimensional bond model appears inapplicable in several cases. The results of a systematic decomposition of the bulk nonlinear coefficients in terms of microscopic bond polarizabilities (β's) will be used to rationalize why one material is superior to another. Recent experimental results on iodates will also be presented.

Introduction

It has recently been shown (*1*) that a three-dimensional model of a chemical bond having nonlinear polarizabilities ($\beta^{\parallel}, \beta^{\perp}$) can be used in a bond additivity scheme in an analogous manner to the linear polarizabilities ($\alpha^{\parallel}, \alpha^{\perp}$) which have been successfully employed for several years (*2*), the respective linear and nonlinear terms (α, β) being the constants which relate the induced dipole moment p to the applied optical field E acting on a given bond, i.e.,

$$p = \alpha E + (1/2)\beta E^2 + \ldots \qquad (1)$$

Since only the IO_3^- and $IO_2F_2^-$ ions have thus far been characterized using a three-dimensional model we therefore extend the calculations to the general oxide classes ABO_x such as $LiTaO_3$, $BaTiO_3$, $H_2PO_4^-$, etc. Our purpose then is to find the constants (β's) for the bonds, which will satisfactorily account for the observed bulk nonlinear coefficients (d's) in terms of only the geometrical factors which relate the bond directions to the crystal axes. It is hoped that if this type of model is successful one might then not only be led to more and perhaps better nonlinear optical materials for device applications but also that new information about the electronic structures of molecules and ions might also be forthcoming.

Results and Discussion

Assuming the point symmetry of a chemical bond can be approximated by C_∞ we thus have four tensor elements (β's) to be determined for any given bond viz.

$$\begin{pmatrix} 0 & 0 & 0 & \beta_{14} & \beta_{15} & 0 \\ 0 & 0 & 0 & \beta_{15} & -\beta_{14} & 0 \\ \beta_{31} & \beta_{31} & \beta_{33} & 0 & 0 & 0 \end{pmatrix}.$$

Further assuming no dispersion i.e. (Kleinman symmetry), we are reduced to only two variables, a parallel bond component ($\beta^{\parallel} = \beta_{33}$) and a perpendicular bond component ($\beta^{\perp} = \beta_{31} = \beta_{15}$), the β_{14} term being zero (*3*).

The various bulk nonlinear optical coefficients (d's) which we shall be relating to our microscopic bond polarizabilities (β's) are

$$d_{33} = (1/V) \sum_i [n_i^3 \beta_i^{\parallel} + 3n_i(1 - n_i^2)\beta_i^{\perp}] \qquad (2)$$

$$d_{31} = (1/V) \sum_i [l_i^2 n_i \beta_i^{\parallel} + n_i(1 - 3l_i^2)\beta_i^{\perp}] \qquad (3)$$

$$d_{32} = (1/V) \sum_i m_i^2 n_i \beta_i^{\parallel} + n_i(1 - 3m_i^2)\beta_i^{\perp}] \qquad (4)$$

$$d_{36} = (1/V) \sum_i [l_i m_i n_i \beta_i^{\parallel} - 3l_i m_i n_i \beta_i^{\perp}] \qquad (5)$$

$$d_{22} = (1/V)\sum_i [m_i^3\beta_i^{\parallel} + 3m_i(1 - m_i^2)\beta_i^{\perp}], \tag{6}$$

where the ith bond has direction cosines $l_i m_i n_i$ (from the positive atom to the more electronegative atom) and sums are taken over each unit cell of volume V.

The basic difference between our approach here and previous calculations and/or decompositions of d's in terms of bond polarizabilities is that here we are treating the bond as a three-dimensional entity (*1*), whereas previous authors either assume $\beta^{\parallel} \gg \beta^{\perp}$ and hence neglect $\beta^{\perp}$ (*4–7*) or their model defines $\beta^{\perp} \equiv 0$ (*8*).

In Table I we tabulate the compounds and their resulting nonlinear bond polarizability terms, i.e., ($\beta^{\parallel}$, $\beta^{\perp}$) as well as the appropriate references to the bulk nonlinear coefficients and structural data. In cases where there were enough nonlinear coefficients to obtain a least-squares fit, the standard error σ is listed to its appropriate β.

Two of the compounds listed in Table I ($NaClO_3$ and $NaBrO_3$) had their respective β's, i.e. ($\beta^{\parallel}$,$\beta^{\perp}$), estimated from only one observed nonlinear coefficient, this was accomplished by assuming $\beta_{I-O} > \beta_{Br-O} > \beta_{Cl-O} > O$ and $\beta^{\parallel}/\beta^{\perp} \sim 3$, as found in the IO_3^- cases (*1*).

The qualitative behavior of the β's (Table I) can be rationalized with the following grossly oversimplified bond model. In Fig. 1a we show how one might expect the linear polarizability (α) of a hypothetical B–O bond to change as the center of "gravity" of the electrons in this bond are moved from B to O. Hence, we see maximum polarizability when the electrons are midway between the atoms and minimum polarizability when the bond is ionic with the electrons either on B or O. Since most elements are more polarizable than oxygen, a more realistic curve might be given by the dotted line. In Fig. 1b we plot the expected bond dipole moment p, again as a function of the electron center of gravity of this same hypothetical B–O bond. Hence we see the minimum dipole for the covalent

TABLE I

B → O	$\beta^{\parallel}(\sigma)$	$\beta^{\perp}(\sigma)$	Compound[a]	Ref.
Be → O	−3.08	−1.04	BeO	(*11, 12*)
Zn → O	−12.4	−3.1	ZnO	(*11, 12*)
S → O	7.0 (1)	2.1 (.3)	$LiKSO_4$	(*11, 13*)
			$Li_2SO_4 \cdot H_2O$	(*11, 13*)
			$BeSO_4 \cdot 4H_2O$	(*11, 13*)
Cl → O	7.05	2.5	$NaClO_3$	(*14, 15*)
N → O	7.3	3.0	$NaNO_2$	(*11, 15*)
P → O	10.4	2.95	KH_2PO_4	(*11, 13*)
Br → O	14.2	4.64	$NaBrO_3$	(*14, 15*)
I → O	34.5 (1.6)	9.65 (.4)	$LiIO_3$	(*11, 16*)
			HIO_3	(*11, 17*)
			$Ca(IO_3)_2 \cdot 6H_2O$	(*6*)
			$K_2H(IO_3)_2Cl$	(*18, 19*)
			KIO_2F_2	(*1, 20*)
Ta → O	51(1)	4.7 (1)	$LiTaO_3$	(*11, 21*)
Nb → O	82(7)	12(3)	$LiNbO_3$	(*11; 22*)
			$Ba_2Na(NbO_3)_5$	(*11, 23*)
			$K_3Li_2(NbO_3)_5$	(*11, 24*)
Ti → O	212	16	$BaTiO_3$	(*11, 17*)

[a] The scale for β's is $\beta \times 10^{-28} m^3 (d_{36} KH_2PO_4)$. In cases with lone pairs of electrons on the B atom such as IO_3^-, ClO_3^-, etc., the β_{LP} is assumed $\sim\beta_{B-O}$ as found in the iodates (*1*).

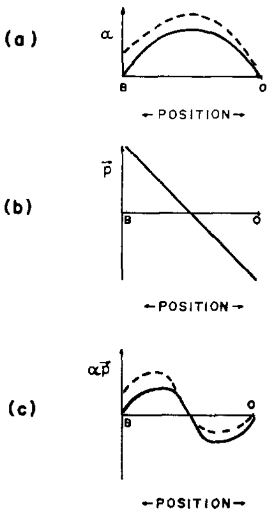

FIG. 1. (a) Expected dependence of linear polarizability (α) on position of the electron center of gravity in a hypothetical B–O bond. The case where $\alpha_B > \alpha_O$ is given by the dotted line. (b) Expected dependence of the bond dipole moment (*p*) on the position of the electron center of gravity in the same hypothetical B–O bond. (c) Product (α*p*) for the same idealized B–O bond which seems to qualitatively describe the behavior of β as seen in Table I.

case and the largest dipole for the two ionic cases. In Fig. 1c we plot the product (α*p*) for the same idealized bond, which seems to qualitatively describe the behavior of β as seen in Table I. Hence we have negative B's for the highly ionic compounds when the center of charge is closer to the oxygen, i.e., (Be^{2+}, Zn^{2+}), and positive β's when the center of charge is closer to the B atom, i.e. (Ti^{4+}, P^{5+}, I^{5+}, S^{6+}, etc.). In the case of intermediate valence compounds such as B^{3+} one can speculate that the anomalously small (*9*) nonlinear coefficients for $LiGaO_2$ might be due to the fact that β(Li–O) is small and opposite in sign to β(Ga–O), hence the sum of the two terms is very nearly a cancellation.

In terms of using the model to predict what new types of materials might be most promising several comments are possible: first from the magnitude of β(Ti–O) and β(Nb–O) one sees that the titanates and niobates clearly make the best candidates; second the low valence metals look the least promising, i.e., Al, Be, Li, etc.; third the high valence compounds (B^{5+}, B^{6+}, B^{7+}) up to the third row of the periodic chart also look poor, hence, fourth the intermediate valence compounds (B^{4+}, B^{5+}) such as Te^{4+}, Sn^{4+}, Sb^{5+}, V^{5+} appear to look the best in terms of untried new materials.

The sign of β relative to the bond dipole moment *p* as shown in Fig. 1 is positive, this indeed may not be the case since O'Hare and Hurst's calculations (*10*) of β's for several diatomic molecules show $\beta \times p < 0$. Another feature of the model is the implication that in SO_4^{2-} for example the center of charge in the S–O bond is closer to the sulfur than to the oxygen. In order to more fully check on these rather fundamental bond concepts one should measure the nonlinear optical properties of molecules where the constituent atoms are small enough to facilitate accurate theoretical calculations.

Note added in proof. A recent microscopic model has shown (*25*) that the relation shown in Fig. 1c viz (β varies as α*p*) should probably contain α to the third power.

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