

CALCULATIONS OF SECOND-ORDER NONLINEAR OPTICAL SUSCEPTIBILITIES IN GLASSES

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INTRODUCTION

The search for new materials of possible application in optical electronics includes a wide range of amorphous glassy materials. Oxide glasses with lead and bismuth oxides, due to the big mass and polarizability of ions Pb and Bi, have interesting properties in nonlinear optics, thus we may consider their application in optoelectronics.

In this work, to analyze the nonlinear optical susceptibilities in lead-bismuth-gallium oxide glasses $\text{PbO-BiO}_{1.5}\text{-GaO}_{1.5}$ using a Green function method which is described in more details in [1-2]. We performed self-consistent functional calculations of the electronic structure. Based on these results, we have estimated the second-order nonlinear optical susceptibilities.

The latter were previously measured using a photoinduced SHG method [3,4,5] and our theoretical results can be compared with these experimental data.

CALCULATIONAL METHOD

Electronic structure calculations have been performed using an extended *ab initio* cluster approximation [1]. Number of atoms of typical cluster were varying between 24500 and 35000 (and even more). Therefore, we have taken into account all possible atomic orbitals (including these of 1s type). We have used a Green function technique to calculate necessary dipole matrix elements.

Let operator L acts on a basis state vector $|\hat{\varphi}\rangle$ being a combination of atomic orbitals which fulfill the following equations:

$$\hat{L}|\varphi\rangle = E|\varphi\rangle. \quad (1)$$

Operator solution to this equation can be written as:

$$|\varphi\rangle = (\hat{L})^{-1}|\Psi\rangle, \quad (2)$$

where $(\hat{L})^{-1}$ is a Green operator associated with L operator and Ψ is a core-like orthonormalized part of φ . If one recalls that a function x is continuous one, then Eq.2 leads after a transformation to the following result :

$$\langle \hat{x} / \varphi \rangle = \int \langle x / \hat{L} \rangle^{-1} |y\rangle \langle y | \Psi \rangle dy = \int \hat{G}(x, y) \Psi(y) dy, \quad (3)$$

where $\hat{G}(x, y)$ is a Green function of \hat{L} operator in x -representation. The operator \hat{L} is written as

$$\left(\hat{L} \right)^{-1} = \int dx dy |x\rangle \hat{G}(x, y) \langle y| \quad (4)$$

A corresponding Green operator for operator $(E - \hat{H})$ is, of course,

$$(E - \hat{H})^{-1} = \hat{G} \quad (5)$$

Assuming $H = \frac{p^2}{2m} + V$, one passes to a coordination representation for which :

$$\int d^3 \vec{r} \langle \vec{r} | E - \hat{H} | \vec{r}' \rangle \langle \vec{r}' | \hat{G} | \vec{r} \rangle = \delta(\vec{r} - \vec{r}') \quad (6)$$

A corresponding differential equation for the Green function G has the form :

$$[\nabla^2 + E - V(\vec{r})]G(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}') \quad (7)$$

An operator solution to the above mentioned equation can be written as :

$$\hat{G}(\vec{r}, \vec{r}') = \sum_n \frac{\langle \vec{r} | n \rangle \langle n | \vec{r}' \rangle}{E - E_n}, \quad (8)$$

To determine the Green operator, we introduce a small imaginary parts $i\varepsilon$ or $-i\varepsilon$ into denominator of expression given by Eq. 8 that results in two Green operators :

$$G^+ = \frac{1}{E - \hat{H} + i\varepsilon} \quad \text{and} \quad G^- = \frac{1}{E - \hat{H} - i\varepsilon} \quad (9)$$

The introduction of the imaginary parts is necessary to fulfill boundary conditions.

The scattering problem has been thus reduced to determination of Schrodinger equation solutions, boundary conditions and positive system energy E . At infinity, we may represent the function $|\Psi\rangle$ by a sum of two functions : a function $|\varphi\rangle$ which describes an incident wave :

$$(E - \hat{H}_0)|\varphi\rangle = 0 \quad (10)$$

and a function φ^+ which corresponds to a scattered wave.

Let us consider the following expression :

$$\langle \vec{r} | \hat{G}^+ | \vec{r}' \rangle = \hat{G}^+ (\vec{r}, \vec{r}', E) = \sum_n \frac{\langle \vec{r} | n \rangle \langle n | \vec{r}' \rangle}{E - E_n + i\epsilon} \quad (11)$$

where $\langle \vec{r} | n \rangle$ are quazi-plane waves for which $E_n = k_n^2$ and $E = k^2$. Integrating with respect to the quazi-wavevector and choosing z-axis direction along a vector $\vec{\rho}$ (where $\vec{\rho} = \vec{r} - \vec{r}'$), one obtains :

$$G^+(\vec{r}, \vec{r}', k) = -\frac{1}{4\pi} \frac{\exp[i\vec{k}(\vec{r} - \vec{r}')] }{[\vec{r} - \vec{r}']} \quad (12)$$

We have used a standard expression for the plane wave (in terms of spheric functions) :

$$\exp[i\vec{k}(\vec{r} - \vec{r}')] = 4\pi \sum_l \sum_m \sum_{m=-l}^l i^l j_l(kr) y_{lm}^k(\vec{r}) y_{lm}^k(\vec{r}') \quad (13)$$

where $j_l(x)$'s are Bessel spheric functions and y_{lm} 's are Legendre spheric functions. Assuming a cluster potential V as a superposition of atomic potentials

$$V = \sum V_\alpha(\vec{r}) \quad (14)$$

it can be shown that :

$$\hat{G} = \hat{G}_0 + \hat{G}_0 \sum_\alpha V_\alpha G_0 + \hat{G}_0 \sum_\alpha V_\alpha G_0 \sum_\beta \hat{G}_0 \quad (15)$$

Considering a t-matrix representation, we may rewrite Eq. 15 as :

$$\hat{G} = \hat{G}_0 + \hat{G}_0 \sum_{\alpha_A} t_\alpha \hat{G}_0 + \hat{G}_0 \sum_{\alpha=\beta} t_\beta \hat{G}_0 + \hat{G}_0 \sum_{\alpha} t_\alpha G_0 \sum_{\alpha=\beta} t_\beta \hat{G}_0 \hat{G}_0 \sum_{\beta \neq \gamma} t_\gamma \hat{G}_0 + \dots \quad (16)$$

A secular equation to the above equations takes the form :

$$| |\delta_{ii} \tau_i^{-1} - k^4 G^+ | | = 0 . \quad (17)$$

We have obtained results which are in practice independent on temperature for different systems. The only temperature dependence can be expected due to Bose-Einstein distribution (see Fig. 1) that is included in final formulas for the nonlinear optical susceptibilities :

$$\chi_{ijk}^{(\alpha,\omega)} = \frac{1}{h^2} \frac{e^3 N^3}{2!} P_{ijk}^{\alpha} \sum_k \sum_{\alpha,\beta} [\frac{\langle 0 | i | \alpha \rangle \langle \alpha | j | \beta \rangle \langle \beta | k | 0 \rangle}{(2\omega + \omega_\alpha)(\omega + \omega_\beta)} + \frac{\langle 0 | j | \alpha \rangle \langle \alpha | i | \beta \rangle \langle \beta | k | 0 \rangle}{(\omega_\alpha - 2\omega)(\omega_\beta - \omega)} + \frac{\langle 0 | j | \alpha \rangle \langle \alpha | k | \beta \rangle \langle \beta | i | 0 \rangle}{(\omega + \omega_\beta)(\omega_\alpha - \omega)}] \quad (18)$$

It is clearly seen that the nonlinear optical susceptibilities are greater for dye doped systems that reflects in fact more essential influence of an electronic non-centrosymmetry. To understand the influence of a possible electron-phonon interaction and a quazi-phonon anharmonicity, we have included electrostatic operators of the electron-phonon interaction into previous equations (within a linear approximation) :

$$V_{ep}(\mathbf{r}_i) = \sum_{m,s} e^2 (t_{ms} \frac{\vec{r}_s - \vec{U}_{ms}}{|\vec{r}_s - \vec{U}_{ms}|^3} - \sum_{m',s'} t_{m's'} \frac{\vec{r}_s - \vec{U}_{m's'}}{|\vec{r}_s - \vec{U}_{m's'}|^3}) \frac{1}{\sqrt{M_{ms}}} \quad (19)$$

where t_{ms} and M_{ms} are effective charges and ionic masses for different vibrations, respectively, indices m,s number corresponding ions and \vec{U} 's are replacements of the ions from their equilibrium positions \mathbf{r}_i .

A corresponding probability of one-phonon transition (induced by the vibrations of frequency Ω_f) is :

$$W^-(\Omega_f) = \frac{4(E_{el} - \Omega_f)^3}{h^2 c^3 H g(\mathbf{r}_i)} B^-(\Omega_f) , \quad (20)$$

where H is a sum of broadenings of lower η -th and upper ξ -th electronic states, E_{el} denotes an energy of electronic transitions, whereas Ω_f is a phonon energy and $g(\mathbf{r}_i)$ is a degeneracy of corresponding electronic levels. A parameter $B^-(\Omega_f)$ can be written in the form [3] :

$$B^-(\Omega_f) = \sum_{n=1}^{\infty} \sum_{\xi=1}^{\infty} \left\{ \sum_{\varphi} \frac{\langle n, n_{\Omega} | V_{\varphi}(r_i) | \varphi \rangle \langle \varphi | \mathbf{d} | \xi \rangle}{E_{\xi} - E_n + \Omega_f} + \frac{\langle n | \mathbf{d} | \varphi \rangle \langle \varphi, n_{\Omega} | V_{\varphi}(r_i) | r, n_{\Omega} - 1 \rangle}{E_{\xi} - E_n - \Omega_f} \right\}^2, \quad (21)$$

where ξ, φ are intermediate virtual states, \mathbf{d} denotes a dipole moment of the electronic transitions. All summations were performed over the intermediate states taking into account the degeneracies of the above mentioned levels. A

notation $\widehat{\theta}$ indicates that considered expressions were averaged with respect to number and directions of phonons. On the other hand, one can write (distinguishing the vibrations) :

$$B^-(\Omega_f) = \frac{\hbar}{\pi} (n_{\Omega} + 1) \sum_{n, \xi} C_{n, \xi}^{\gamma}(\mathbf{r}_{\lambda}^{\Delta}) \cdot C_{n, \xi}^{\gamma'}(\mathbf{r}_{\lambda}^{\Delta}) \cdot \text{Im} G_{\Delta\Delta}^{\gamma'}(\mathbf{r}_{\lambda}^{\Delta}, \Omega_f^2),$$

$$C_{n, \xi}^{\gamma}(\mathbf{r}_{\lambda}^{\Delta}) = \sum_{\varphi} \left\{ \frac{\langle n | V_{\varphi} | i \rangle \langle \varphi | \mathbf{d} | \xi \rangle}{E_{\xi} - E_n} + \frac{\langle n | \mathbf{d} | \varphi \rangle \langle \varphi | V_{\varphi}(r_i) | \xi \rangle}{E_{\xi} - E_n} \right\}, \quad (22)$$

where $G_{\Delta\Delta}^{\gamma'}(\mathbf{r}_{\lambda}^{\Delta})$ are Green functions and γ 's are coordination sphere numbers. To calculate the Green functions, we have performed summations over 1120 points within the effective sphere :

$$G_{\Delta\Delta}^{\gamma'}(\mathbf{r}_{\lambda}^{\Delta}, \Omega_f^2) = \sum_{\Omega_f} \frac{K_{\Omega_f}(\mathbf{r}_{\lambda}^{\Delta}) K_{\Omega_f}^{\gamma'}(\mathbf{r}_{\lambda}^{\Delta})}{\Omega_f^2 - \Omega_f'^2 - i\delta}, \quad (23)$$

where the coordinates were determined using lattice dynamics matrices for the quazi-phonons in 13450 points within the effective sphere. To take into account an influence of neighbouring molecules, we have introduced an effective local Lorentz field which effectively influences a scaling of eigenvalues and eigenvectors.

We have used a Dyson equation with the electron-phonon potential as a perturbation that leads to a defect of charge and mass :

$$G_{\Delta\Delta}^{\gamma'} = G_{\Delta\Delta}^{\gamma'}(0) + G_{\Delta\Delta}^{\gamma'}(0) U G_{\Delta\Delta}^{\gamma'}(1), \quad (24)$$

where $G_{\Delta\Delta}^{\eta'}(0)$ and $G_{\Delta\Delta}^{\eta'}(1)$ are corresponding Green functions for the unperturbed and perturbed systems, respectively. A relation between real and imaginary parts of the Green functions were determined using dispersion relations. The electron-phonon perturbation can essentially improve calculational results.

RESULTS AND DISCUSSION

Calculated results for electronic density of states are presented in Fig. 1. A substantial contribution of 6s and 6p Pb states to the total density of states (DOS) should be noticed in an energy region between -5 eV and 5 eV. On the other hand, highly localized 2s O states begin to play essential role in an energy region near -8 eV and -10eV.

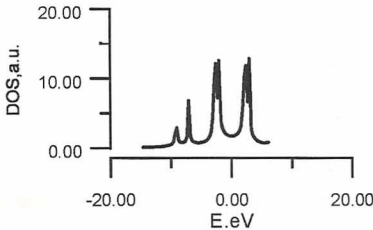


Figure 1. Theoretically calculated electronic density of states (DOS, in arbitrary units) as a function of energy E for PbO-BiO_{1.5}-GaO_{1.5} glasses.

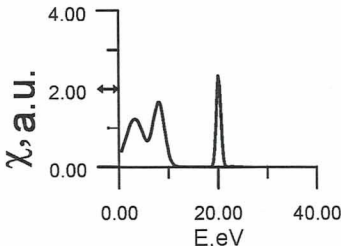


Figure 2. Calculated averaged nonlinear optical susceptibility, (in arbitrary units) as a function of energy E for PbO-BiO_{1.5}-GaO_{1.5} glasses.

A dispersion of the nonlinear optical susceptibility of PbO-BiO_{1.5}-GaO_{1.5} glasses has been predicted that is depicted in Fig. 2. The 4sGa-2pO chemical bonds contribute to the total effect in more than 60 % .

Therefore, a content change of these components can lead to an essential increase of the total nonlinear optical susceptibility. Another possibility arises when introducing impurities into the glass.

CONCLUSIONS

The presented above results have shown advantages of Green function technique for estimations of the nonlinear optical susceptibilities. In particular, our calculations have revealed the essential contribution of delocalized states to nonlinear optical susceptibilities. Moreover, this calculational technique allows us to predict possible variations of material parameters in required directions that can be very important from a technology point of view. Therefore, one can use this approach in materials engineering of glasses in order to obtain desirable properties [6].

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