Nonlinear optical properties of tellurium oxide nanoclusters

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Abstract. The finite field method using ab initio hybrid functional approach was applied to estimate nonlinear properties of the cluster based on paratellurite crystal structure. The good agreement was found with previously reported data. The method demonstrate high efficiency in prediction of nonlinear properties for a wide ensemble of sufficiently large polyatomic clusters.

1. Introduction
Practical and theoretical interest to the crystalline and glassy tellurium oxides was primarily stimulated by their outstanding nonlinear optic (NLO) properties. Attempts to understand the origin of the remarkable NLO properties of TeO2-based glasses have been undertook in a series of theoretical studies. As soon the synthesis of systems with well-defined structural, opto-electronic and transport properties under full control is difficult, the use of a computational modelling based on the quantum-mechanical calculations could clarify the role played by various structural units and electronic states.

In order to the better tellurite glasses outstanding NLO properties understanding, theoreticians focused their attention on the crystals with the similar chemical and atomistic constitution. The NLO characteristics have been calculated for several tellurium oxide crystals [1–3]. It was stated that such calculations are very time-consuming since require to involve sophisticated computational methods (GWA, DFT+U, etc.). Another fundamental limitation of the “crystalline” approach concerns the inability (at least the encumbrance) to vary chemical composition in the modifier effect studying, which is of primary importance for the synthesize the real samples.

An alternative theoretical approach deals with the quasi-molecular polyatomic clusters destined to mimic the local structural units of the glasses. These attempts [4–6] faced with another problem: the optimized structures of the clusters turned out rather multifarious and close in energy. This fact hampered the choice of the most representative cluster structure.

A new method combining advantages of the “crystalline” and cluster approaches is discussed in the present paper. The method is based on use of a finite cluster obtained by cutting-out a part of the infinite periodic crystal. The cluster is formed as a supercell containing a dozen of the unit cells. Positions of atoms in the cluster are fixed as they were obtained from the crystal
geometry optimization. The broken valence bonds are bunged by hydrogen atoms. Positions of the hydrogen atoms are optimized at keeping fixed the internal heavy atoms. Electronic structure of thus obtained “cut-and-wrapped” cluster is studied by using the methods and computational programs designed for the molecules.

The proposed approach essentially facilitates the problem as far as calculation of electronic structure of a molecule is much simpler and the results can be interpreted in terms of localized molecular orbitals. At the same time, a justification of the approach is not an easy task:

- One have to study dependence of results on the size and shape of the cut supercell (optimized);
- It is necessary to estimate and to extract the contributions of the surface hydrogen atoms to the calculated NLO characteristics.

In order to satisfy these statements the validation of the approach is required by using the well studied modal compound. The paper reports formulations of the method to calculate NLO properties of nanoclusters and the validation of the method confirmed in the case of paratellurite $\alpha$-TeO$_2$ crystal, which was precisely studied before [3].

2. Computational details

The calculations performed within density functional theory (DFT) with the localized atomic functions (LCAO) basis using CRYSTAL and Gaussian16 software packages [7, 8]. The one parametric hybrid functional PBE0 [9] method to rule the mixing of exact Hartree-Fock (HF) exchange and DFT exchange and correlation was used with portion of exact exchange equal to 16.667%. The consistent gaussian basis set of triple-zeta valence with polarization quality [10] for oxygen atoms was used in the calculations. Due to complex electronic structure, pseudopotential method was applied for Te atoms with gaussian double-valence basis set [11]. Kohn–Sham equations are solved iteratively to self-consistency within $3 \times 10^{-10}$ eV. The Monkhorst–Pack scheme [12] for $6 \times 4 \times 6$ k-point mesh was applied for the BZ sampling in the case of $\alpha$-TeO$_2$ crystal structural and NLO properties calculations. To obtain ground state properties, lattice parameters and fractional positions of atoms have been fully optimized. Cell relaxations were achieved with the convergence criterion for forces on atoms less than $5 \times 10^{-5}$ Ha Bohr$^{-1}$. The NLO properties of single crystal $\alpha$-TeO$_2$ were calculated as a fourth order derivative of the total energy with respect to the various components of the electric field by using Coupled-Perturbed Kohn-Sham (CPKS) formalism as implemented in the CRYSTAL code [7, 13].

3. Results and discussion

The $\alpha$-TeO$_2$ crystal is formed by chains of TeO$_4$ disphenoids. There are two short equatorial Te-O$_{eq}$ and two long axial Te-O$_{ax}$ bonds [14]. The first step of our research was devoted to obtaining of the fully relaxed structure by performing geometry optimization within PBE0 hybrid functional method using CRYSTAL software package. The axial distance for Te-O$_{ax}$ bonds was found to be equal to 2.137 Å along with equatorial bond equal to 1.923 Å, which well reproduce experimental ones (2.122 Å and 1.876 Å for axial and equatorial bonds respectively). Then the cluster of the size 8 unitcells by constructing $2 \times 2 \times 2$ supercell was “cut out” from the crystal, thus the total number of TeO$_2$ molecules is 36. Then the edge oxygen atoms were terminated by hydrogens to preserve charge neutrality, and the atomic positions of H atoms was found by relaxation fixing the other atomic positions. The resulted cluster is plotted in figure 1.

In order to obtain nonlinear optical properties of the cluster the following formalism was applied. The total energy E of the system can be expanded into perturbative series of the field components (denoted by indices $t,u,v \ldots$) [15]

$$E(\mathcal{E}) = E(0) - \sum_t \mu_t \mathcal{E}_t - \frac{1}{2!} \sum_{tu} \alpha_{tu} \mathcal{E}_t \mathcal{E}_u - \frac{1}{3!} \sum_{tuv} \beta_{tuv} \mathcal{E}_t \mathcal{E}_u \mathcal{E}_v - \frac{1}{4!} \sum_{tuvw} \gamma_{tuvw} \mathcal{E}_t \mathcal{E}_u \mathcal{E}_v \mathcal{E}_w, \quad (1)$$
where $\mu$ is dipole moment, $\alpha$ – linear polarizability, $\beta$ – hyperpolarizability, and $\gamma$ – second hyperpolarizability. Hence the dipole moment of the cluster is given by:

$$\mu_t = \mu_0 + \sum_{v=1}^{3} \alpha_{tv} \mathbf{E}_v + \frac{1}{3} \sum_{v,u=1}^{3} \beta_{tuv} \mathbf{E}_v \mathbf{E}_u + \frac{1}{6} \sum_{v,u,w=1}^{3} \gamma_{tuvw} \mathbf{E}_v \mathbf{E}_u \mathbf{E}_w. \quad (2)$$

The permanent electric dipole moment $\mu$ of the cluster is related to macroscopic polarization vector as $\mu = V \mathcal{P}$, where $V$ is volume of the cluster and $\mathcal{P}$ is given by equation 2.

$$\mathcal{P} = \varepsilon_0 (\chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E} \cdot \mathbf{E} + \chi^{(3)} \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E}), \quad (3)$$

The field in eq.2 should be specified as the local field – that is the effective electric field that acts on the molecule, while the electric field in eq.3 is macroscopic one. The local field is related to macroscopic one as $E_{\text{loc}} = E_{\text{macro}} f_L$, where $f_L$ is a Lorentz factor equal to $f_L = 1 + \frac{1}{3} \chi^{(1)}$ [16]. Therefore, by applying the value of local field from eq. 2, 3 one can find the relations for nonlinear susceptibilities expressed in terms of linear and hyperpolarizability [5]:

$$\chi^{(1)} = \frac{\alpha_s}{\varepsilon_0 V_s} \left( 1 - \frac{\alpha_s}{3\varepsilon_0 V_s} \right)^{-1}, \quad \chi^{(2)} = \frac{\beta_s}{2\varepsilon_0 V_s} \left( 1 - \frac{\alpha_s}{3\varepsilon_0 V_s} \right)^{-2}, \quad \chi^{(3)} = \frac{\gamma_s}{6\varepsilon_0 V_s} \left( 1 - \frac{\alpha_s}{3\varepsilon_0 V_s} \right)^{-3}, \quad (4)$$

where $\varepsilon_0$ is the vacuum permittivity, $\alpha_s$ is specific linear polarizability, $\beta_s$ and $\gamma_s$ are specific first and second hyperpolarizability of a given cluster correspondingly, and the $V_s$ value can be specified as the specific volume (per one structural unit TeO$_2$).

The orientation of the cluster in Cartesian coordinates was set with dipole momentum direction along $z$ axis. The set of polarization calculations by applying electric field along $x,y$ and $z$ axis were performed to calculate hyperpolarizability. The first hyperpolarizability is $\beta(\mathcal{E}_i) = -\frac{\partial^3 E}{\partial \mathbf{E}_i}$ i.e. the third order derivative of total energy at each electric field applied. And the second hyperpolarizability is the fourth order derivative of the total energy with respect to electric field, hence the derivative of hyperpolarizability $\beta$ with respect to electric field $\gamma_{tuvw} = \frac{\partial \beta_{tuv}}{\partial \mathbf{E}_w}$. Thus by numerical differentiation using values of hyperpolarizability for two fields $\beta(\pm \mathbf{E})$, one can immediately estimate the diagonal and non-diagonal elements of hyperpolarizability tensor. The mean value of hyperpolarizability is calculated using equation:

$$< \gamma > = \frac{1}{5} (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xyyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz}). \quad (5)$$

Figure 1. The $\alpha$-TeO$_2$ like cluster in two perpendicular projections. Brown balls – tellurium atoms, red and white balls is oxygen and hydrogen atoms respectively.
All calculations were performed using atomic units, the calculated values for second order hyperpolarizability was obtained equal to $<\gamma> = 8.649711E+05$ a.u. and using eq. (4) the third order nonlinear susceptibility in SI units was found equal to $\chi(3) = 136.7 \times 10^{-22}$ m$^2$ V$^{-2}$, such value is close to the one calculated for single crystal $\alpha$-TeO$_2$ by CPKS method as implemented in CRYSTAL code [13] using the same functional, basis set and structural parameters $\chi(3) = 93.4 \times 10^{-22}$ m$^2$ V$^{-2}$, and well reproduces the previously reported value $\chi(3) = 119.59 \times 10^{-22}$ m$^2$ V$^{-2}$ [3]. There is overestimation of the $\chi(3)$ value for the cluster with respect to $\alpha$-TeO$_2$ crystal, which is due to underestimation of the band gap value (HOMO-LUMO energy difference $E_g = 3.38$ eV), while value for single crystal is found $E_g = 3.75$ eV [3]. Such discrepancy could be explained by influence of O bonds terminated by hydrogen atoms. The value of the second order susceptibility was found to be rather small $\chi(2) = 0.23$ pm V$^{-1}$ due to the fact that the second order nonlinearity in static limit is forbidden for paratellurite crystal by Kleiman symmetry [16].

Finally, the ab initio method of nanocluster NLO properties calculation was postulated and validated. The approach is simple and obtains sufficiently accurate results with a reasonable computational costs.

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