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Interface effects on the NLO properties of guest–host materials

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Electro-optical properties of silicon carbide (SiC) nano-sized clusters embedded into three different polymeric matrices, i.e., poly(methyl methacrylate, poly-N-vinylcarbazole and polycarbonate were investigated. Electric properties of SiC were calculated using time-dependent DFT methods considering an isolated cluster and environmental effects. The concept of the polymeric influence on optical properties of chromophores was executed by the local electric field approach. Electric field created by charge distribution of the surrounding polymer was calculated using guest–host structures obtained by the molecular dynamics simulations. Optical properties of SiC situated in polymeric environments differ from those of free clusters. It is seen more significantly for the hyperpolarizability than for the polarizability. The spatial distribution of SiC in the matrix depends on the kind of polymer and gives an important influence on the obtained local electric field value. The Si–C distances do not change with variation of the polymeric matrix. The geometry of 3C–SiC is very stable and does not change during MD simulations performed at 300 K.

Key words: *composite material*; *guest–host material*; *nonlinear optics*; *electro-optics*; *SiC*

1. Introduction

In the recent decades, increasing interest has been paid to nonlinear optics (NLO) in hybrid nanomaterials due to a possibility of incorporation of semiconducting nanograins as chromophores in a polymeric medium [1–3]. The importance of semiconductor nanocrystals consists in exhibition of size-dependent electronic and optical properties, significantly different from those of the corresponding bulk-like lattice [4]. The strategy to develop efficient NLO composite materials requires appropriate matrices in

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order to enhance the physical responses. Furthermore, the polymeric matrix should assure the photo-transparency, mechanical hardness and thermal stability. On the other side, the electrostatic influence coming from a host polymer and the intermolecular forces can affect external structure of guest grains and change electric molecular properties. Moreover, it is necessary to investigate experimentally difficult environmental effects (polymer–nanograin) on the optical properties of the nanocomposites. For this purpose, molecular simulations are powerful methods to evaluate the guest–host interaction and to separate their individual contributions to the overall NLO response. Macroscopic susceptibility of a guest–host system is determined by microscopic polarizabilities and hyperpolarizabilities of the constituents and their distribution. In the frame of the local field theory, linear and nonlinear macroscopic susceptibilities are related to molecular properties by local field factors. The local field approach may be taken into account to analyse the nature of the molecular environment of nanograins and to calculate macroscopic electro-optical (EO) properties of composite materials.

In the present work, silicone carbide (SiC) nanograins were chosen as inorganic chromophores because composite materials consisting of the SiC nanocrystallites embedded within the photopolymer olygoetheracryalte matrices were proposed as promising NLO materials [5]. From the wide variety of SiC polymorphic structures, the 3C–SiC nanograins were studied and the influence of organic host matrices on their optical properties was examined. Poly(methyl methacrylate) (PMMA), poly-N-vinylcarbazole (PVK) and polycarbonate (PC) were chosen as hosts due to their good optical and thermomechanical properties. The results presented in the paper include only theoretical investigations of polymeric influence on NLO properties of SiC chromophores.

The guest–host systems were built using molecular dynamic (MD) simulations method and the full atomistic modelling of the composite materials was achieved. The first order nonlinear optical hyperpolarizabilities $\beta(-\omega; 0, \omega)$ for the SiC nanograins were calculated using the density functional theory (DFT) methods. The structures of modelled systems were used to analyse environmental effects of polymeric matrices on the optical properties of the SiC chromophores. The macroscopic susceptibilities of the considered systems were computed using the local field theory and the obtained results have been compared with the experimental data [1, 2]. In the present work, we tried to simulate the physical process to assess the impact of main structural fragments on the electronic properties of the composite materials using time-dependent DFT (TDDFT) simulations together with the method of MD. Additionally, it was found that polymer environment reconstructs the surface of the SiC nanograin, contributing critically to the NLO properties of these hybrid materials.

The physical insight into the interface effects obtained by numerical methods was the goal of the presented paper and as a support for the theoretical models, we considered the Pockels effect demonstrated experimentally in SiC-based hybrid materials.

2. Molecular dynamic simulations

Three host–guest systems were simulated, namely SiC/PMMA, SiC/PC and SiC/PVK structures. Three equivalent starting structures, for each system, were generated using Hyper-Chem program package [6]. A unit cell of each investigated system consisted of one chain of PMMA 90-mer with molecular weight 9012.58 amu, one PC 50-mer chain (12716.21 amu), one PVK 50-mer chain (9664,45 amu), respectively and one SiC cluster. The structures of the polymers are presented in Fig. 1.

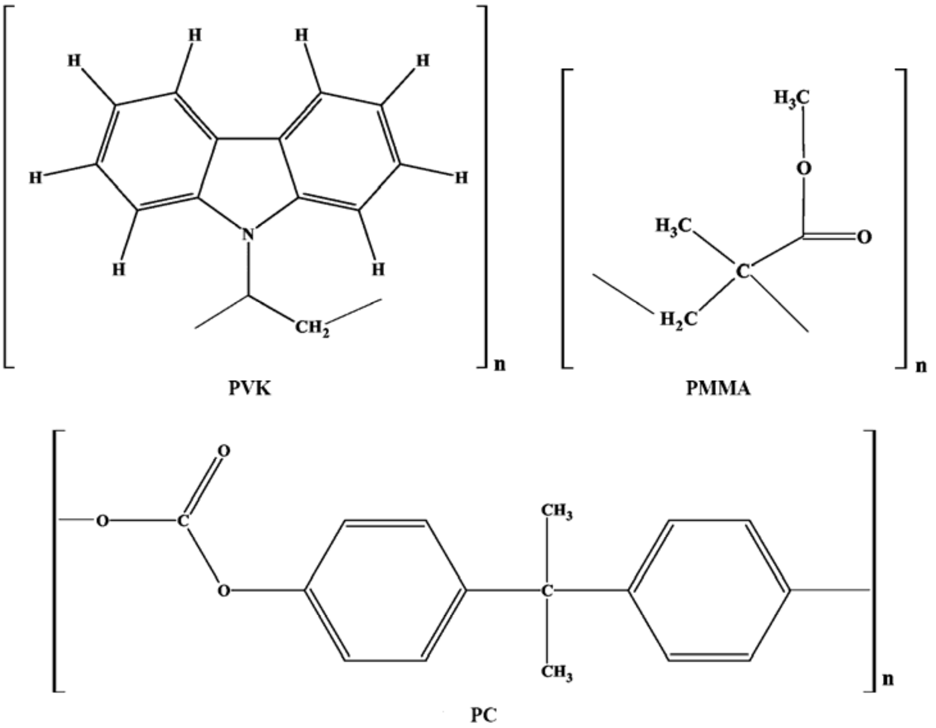

Fig. 1. Formulae of the PVK, PMMA and PC structural units

The SiC cluster (the mass of 4330.48 amu), was built with the cubic crystalline arrangement consisting of 108 SiC pairs. Every simulated unit cell of investigated structures was cubic with the edge length of 27.10 Å, 29.99 Å, 28.34 Å for the SiC/PMMA, SiC/PC and SiC/PVK systems, respectively. The density of each system was 1.20 g/cm^3 and corresponded to the solid state densities of considered matrices. The mass fractions of SiC embedded into the polymeric environment were 48.05 wt. % for PMMA/SiC, 34.05 wt. % for PC/SiC and 44.81 wt. % for PVK/SiC systems.

MD simulations were performed using the GROMACS software [7]. A leap-frog algorithm was used to integrate Newton's equations of motion [8]. The potential energy was computed as a summation of the contributions of bonded terms and non-bonded interactions such as the Lennard–Jones 12–6 and Coulomb potentials. Bonded interactions are based on a fixed list of atoms and non-bonded ones on a dynamic list. The atomic charges of the system constituents were obtained using DFT calculations described below. The pair list was updated after every step of MD run. To make the neighbour list, the grid search algorithm was used with the cut-off parameter equal to 1.3 nm. Bond interactions were represented by harmonic potentials, while angle and dihedral distortions were modelled by a simple cosine function. The potential function of the modelled system is described via the all-atom consistent valence force field (CVFF) [9]. The parameters of SiC_4 and CSi_4 tetrahedral bonding potentials are given in [10]. The CVFF force field has been successfully used to model a wide variety of biophysical, crystal and guest–host systems [11–13].

At first, geometry of each investigated system was optimized using energy minimization employing the steepest descent method with a convergence criterion of $10\ \mathrm{kcal\cdot mol^{-1}\cdot Å^{-1}}$. All MD simulations were conducted at constant number of particles, volume and temperature (NVT ensemble) by applying periodic boundary conditions. Each investigated system was first evaluated during 2 ns at 300 K, using the time step of 1 fs to allow sufficient equilibration of the system. These data were not used in a subsequent analysis. The stability of the total energy was reached after about 1.5 ns of MD run. Then, the simulations were ran again at 300 K, with the time step of 1 fs and the coordinates were stored every 1000 steps. Equilibration of temperature to the desired value of 300 K was carried out in increments of 2 K using the Nose –Hoover thermostat [14]. A cut-off of 1.3 nm was used for the van der Waals interaction. The particle mesh Ewald (PME) summation [15] was employed for the electrostatic long-range interactions. The cut-off distance for the integrating coordination numbers was larger than the nearest-neighbour distance of a perfect 3C–SiC crystal structure.

3. Quantum-chemical computation

Optical properties of the SiC nanograins were calculated in the finite-cluster and local field modification approaches using geometries of isolated 3C–SiC structure of 216 atoms. Quantum-chemical computations reported in this paper were performed using the Amsterdam Density Functional (ADF) package [16] implementing Slater-type basis sets. All calculations were performed with the standard double ζ basis sets available in ADF, described in the references. The polarizability α and first hyperpolarizability β were calculated using ADF-RESPONSE module [17] within the frame of time-dependent DFT (TDDFT) theory. The local density approximation (LDA) for the potential and kernel was used, which compose the local Slater exchange functional [18] and the uniform electron gas local correlation functional due to Vosko, Wilk, and Nusair (VWN) [19]. All the clusters were rotated to align maximal ground state dipole moment along the Z-axis.

In the frame of the local field theory, linear and nonlinear macroscopic susceptibilities are related to molecular properties by the local field factors. In the discrete local field theory, the local fields are computed considering the molecular environment rigorously. The intensity of the created electric field depends on the arrangement of the polarized molecules around the point of interest, in our case in the centre of mass (COM) of the SiC cluster. Using the results of MD simulations, the guest–host structures were considered to calculate the electrostatic interaction between the polymer and SiC cluster. The local electric field was calculated for each system in the COM of SiC, for each snapshot of the MD simulations via the boundary condition and then averaged. The influence of the next neighbour cells was taken into account up to the difference ΔF between two calculated electric fields less than 10^{-3} GV/m. The calculated electric fields for all considered systems are collected in Table 1. In order to calculate electrostatic intermolecular interactions, the data from the last 0.5 ns of MD run were considered. The obtained electric fields were applied to predict the linear and nonlinear response of investigated composites as it was developed for the poled guest–host polymer systems [20].

Table 1. Average local fields (F) on COM of SiC in PMMA, PVK and PC matrix

System	F_x [GV/m]	F_y [GV/m]	F_z [GV/m]	F [GV/m]
PMMA/SiC	–0.34	–0.68	0.99	1.28
PVK/SiC	–0.18	–0.81	–0.93	1.25
PC/SiC	5.16	–4.44	11.98	13.78

4. Results and discussion

The MD resulting structure of SiC cluster can be characterized by its radial distribution function (RDF). The highest, considered distance between investigated groups is equal to the half of the unit cell length. The atomic RDFs of Si and C atoms at the end of MD simulations are presented in Fig. 2. The maximum of presented RDFs, for each investigated polymeric matrix, is located at 0.189 nm, corresponding to the nearest-neighbour distance in 3C–SiC structure. This peak describes Si–C bonds, and is related to a C–Si–C configuration. In the SiC solid crystal, the atoms are located in well-defined lattice-site equilibrium positions, around which they perform vibrations with relatively small amplitudes of motion with slight variation of interatomic distances. The second peak of the curves is centred at the distance of 0.378 nm, which is related to Si–C farthest neighbour distance. Computed RDFs of Si–C distances do not change with the variation of the polymeric matrix. Thus one can conclude that the geometry of 3C–SiC is very stable and average distances between Si and C atoms do not change during MD simulations performed at 300 K, which is very far from the melting point of SiC. Internal Si–C structure of the investigated clusters is their intrinsic property and does not change under influence of considered polymeric matrices.

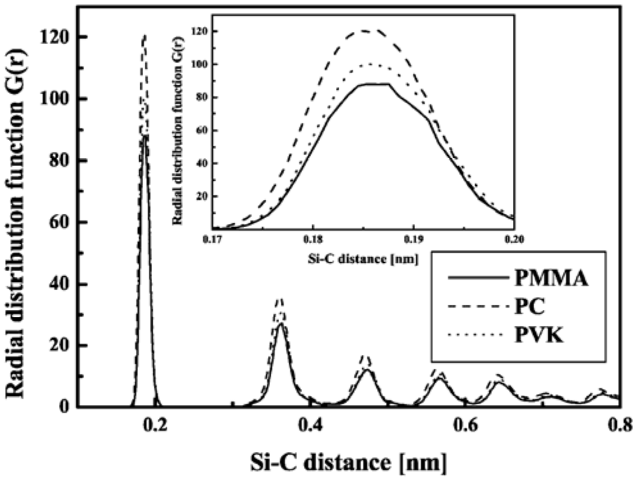

Fig. 2. Atomic radial distribution function $G(r)$ between the Si and C atoms of the 3C–SiC clusters embedded into PMMA, PVK and PC polymeric matrix

The principal goal of the investigation was not to simulate the structure of SiC but rather to determine their polymeric environment. Spatial distribution of the SiC clusters in polymeric matrix was investigated basing on intermolecular RDFs which were calculated between last Si-C surface atoms of SiC structure and determined groups of considered polymers. For the PMMA the COM of four groups were used, namely: methyl group bonded to the backbone carbon atom, methyl group bonded to COO, COO group and CH_2. The RDFs between SiC nanograin and PC polymer were calculated for the COM of four polymeric groups: both of two benzene rings, $C\text{-}(CH_3)_2$ group and C=O group. For the PVK also four groups were chosen, namely: COM of both of two benzene rings, COM of CH_2 group and the N atom. In order to show spatial distribution of the SiC nanograin in polymeric environment, only the nearest distances between the cluster and polymeric groups are drawn (Fig. 3). The presented RDF of the SiC–PMMA distance has been calculated for the methyl group bonded to COO. It is the nearest polymeric group to the SiC cluster with the distance equal to 0.4 nm. For the PC and PVK, as the RDF describing the nearest SiC–matrix distances, benzene rings and the carbazole group were taken, respectively. The SiC cluster situated in the PC matrix is located closer to the polymer than it was found for PMMA, the calculated distance being equal to 0.34 nm. A similar distance was found between the SiC cluster and PVK. The first RDF peak related to the SiC–PVK distance is very broad, which means that nanograins located closer to the polymer chain than 0.34 nm may be found. One can conclude that a free space around SiC cluster in the PVK matrix is the lowest as compared to PMMA and PC. All observed RDFs are typical of amorphous structures. No long-range order exists for considered systems but one can see that the PC polymeric matrix with SiC nanoclusters is more ordered than the two other investigated systems. A free space around SiC clusters incorporated into PMMA matrix is the largest among all investigated matrices and has the same value as it was calculated for variety of organic chromophores [11].

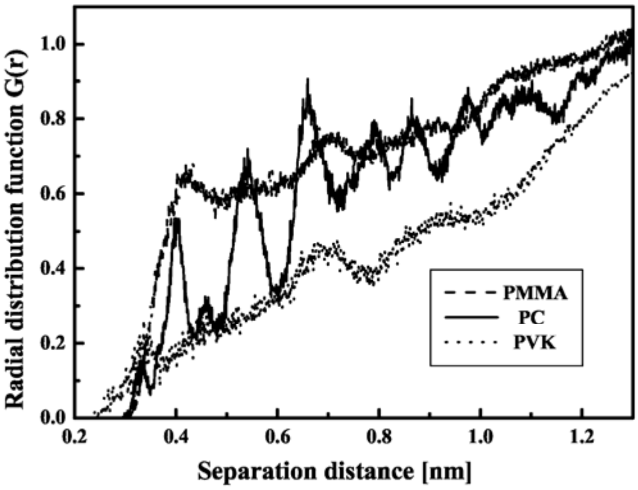

Fig. 3. The function of intermolecular radial distribution for the last Si–C surface atoms of SiC nanograins and the polymer chains

Rotation of the SiC nanorgains in PMMA is relatively easy as compared to the other systems. On the other hand, a free rotation motion of SiC is allowed in PMMA matrix, hence the relaxation of the aligned nanograins should be easy and fast.

Table 2. Molecular electric dipole moments μ, HOMO-LUMO energy splitting $\Delta E_{\text{HOMO-LUMO}}$, polarizability α and hyperpolarizability β of the SiC cluster calculated in vacuum and in a polymeric environment (λ = 633 nm; 1 au = 0.16487×10^{-40} $C^2\cdot m^2\cdot J^{-1}$ for α and 0.32066×10^{-52} $C^3\cdot m^3\cdot J^{-2}$ for β)

Molecule	μ [D]	$\Delta E_{\text{HOMO-LUMO}}$ [eV]	α_{av} [a.u.]	$\beta_{vec}(\omega;0,\omega)$ [a.u.]
SiC	5.86	3.40	2069.2	743.6
SiC in PMMA	17.54	3.30	2071.1	1951.5
SiC in PVK	9.19	3.26	2069.4	897.4
SiC in PC	69.82	1.31	2098.3	235400.0

In Table 2, electric properties of the isolated SiC clusters calculated by DFT method are presented. The obtained energy splitting $\Delta E_{\text{HOMO-LUMO}}$ value for the SiC isolated grain is in agreement with the work of Reboredo et al. [21] and is blue-shifted as compared to the bulk 3C–SiC because of small cluster size. The $\Delta E_{\text{HOMO-LUMO}}$ and μ values calculated for the SiC clusters located in polymeric matrix demonstrate that the environmental effect narrows the energy gap of the SiC clusters and increases the static dipole moment. The most important change was found for the SiC embedded into PC matrix due to a high local electric field created by the polymer in the COM of the investigated cluster (see Table 1). Generally, each considered polymer matrix delocalizes charge density of the semiconducting cluster. One can conclude that all investigated polymers should be appropriate to use them like matrices keeping the SiC clusters.

Polarizabilities α and hyperpolarizabilities β related to the electrooptical effect of the SiC clusters were calculated using the Hartree-Fock and time-dependent DFT approaches at $\lambda = 0.633$ μm. The calculations are performed for the isolated molecule as well as for those embedded into polymeric matrix. Environmental effects are taken into account via the local field theory using the point-dipole approach and the obtained results are compared with the experimental data published earlier [1, 2]. The obtained polarizabilities α and hyperpolarizabilities $\beta(\omega;0,\omega)$ are presented in Table 2. Even taking into account the differences observed for the local field calculations, considering investigated systems (see Table 1), the environmental effect related to the linear optical properties can be neglected for all matrices. The average value α_{av} calculated in the respective local field is about 1% higher as compared with the polarizability calculated for the isolated molecule in any polymeric environment. One can see the tendency for the calculated local field to be parallel to the molecular dipole moment direction. The absolute field values obtained for the PMMA and PVK matrices are much lower than those calculated for the molecular crystals [22] but comparable with previously investigated other guest–PMMA systems [20]. The intermolecular SiC–PC interactions are many times higher than for the PMMA and PVK matrices.

The environmental effect is more distinct for the NLO properties that for the linear ones. All considered matrices increase the $\beta(\omega;0,\omega)$ value of the 3C–SiC clusters. The observed effect is the most distinct for SiC-PC system because of high local field in COM of cluster. The effect of the local field on the liner polarizability is negligible for all investigated systems but should be considered calculating NLO properties. In Figure 4, the experimentally obtained effective EO parameters r_e are presented for the 3C–SiC nano-sized grains embedded in polymeric matrices of various kinds (bars). The set-up used in the experiment is described in details in previous works [1, 2]. EO coefficients are obtained for the poled guest–host systems. These results are compared to the hiperpolarizability $\beta(\omega;0,\omega)$ related to the EO effect, computed within the local field approach. In practice, this comparison is not straightforward. The r_e parameter depends not only on the effective hiperpolarizability $\beta(\omega;0,\omega)$ of considered molecule but also on the unit cell volume, density of active molecules and the order parameters of the system. We compare only the tendency of changes of both investigated properties. One can conclude that the theoretically obtained data are in a good agreement with the experimental results. A very high value of the $\beta(\omega;0,\omega)$ obtained for the SiC–PC system can be practically decreased by the relatively difficult orientation of the SiC nanograins because of low free space around the chromophores. The order parameters obtained for the SiC–PVK system will probably decrease the EO molecular output signal.

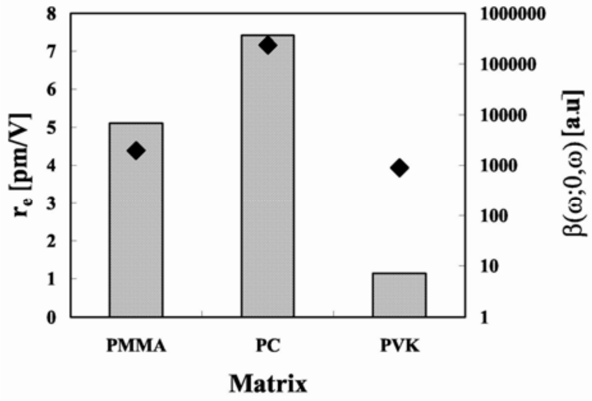

Fig. 4. Linear effective EO parameters r_e experimentally obtained for various kinds of polymeric matrices (bars) and hiperpolarizability $\beta(\omega;0,\omega)$ calculated via the local field theory (diamonds)

The EO properties of the considered systems can be confirmed by more detailed MD simulations of the electrically polled systems, however, the calculations of the macroscopic optical properties should be supplemented with the Lorentz field factor calculations. This approach can be combined with the permanent field effect on the surface-perturbed molecular response. It will be the subject of future work.

5. Conclusions

The EO properties of the composite materials were investigated by the MD study of the SiC–polymer structure. We attempted to describe the factors affecting microscopic molecular NLO properties of the SiC clusters embedded in PMMA, PVK and PC matrices.

The distance between SiC clusters and the polymer depends on the kind of polymer. By the study of the SiC–PMMA system and comparing the obtained results to the previously reported data one can conclude that the location of the chromophore in PMMA matrix is an intrinsic property of the polymer used and is not affected by the organic or inorganic dopants. Free space around SiC cluster in PVK matrix is the lowest as compared to the PMMA and PC. The alignment of the SiC nonograins in PVK is more difficult than in PC or PMMA matrix. Concerning the free space around 3C–SiC the SiC–PMMA system is not stable because of easy back relaxation of the chromophores. The Si–C distances do not change via the variation of the polymeric matrix. The geometry of 3C–SiC is very stable and does not change during MD simulations performed at 300 K.

The optical properties of the SiC clusters were calculated via the local field approach. The environmental effect on the molecular polarizability is not significant and may be neglected during the quantum-chemical calculations. The local field effect is much more pronounced for the NLO properties of SiC and may not be omitted. The tendency of the $\beta(\omega;0,\omega)$ changes via the variety of polymeric matrices by the simple local field approach can be reproduced. All considered polymeric matrices increase the NLO properties of SiC nanosized crystals.

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