Band energy approach and nonlinear optical phenomena in large-sized nanoparticles

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Abstract— This report presents principal optical properties of semiconducting large-sized nanocrystalline (LSNC) material with thickness within 10–50 nm range. A quantitative parameter for description of the LSNC state is introduced. Influence of the surrounding polymer matrices on the properties of the LSNC is shown. Role of the surrounding polymer matrix background in the manifestation of material optoelectronic properties is studied. Superposition of long-range ordering with the localized nano-quantized effects is analyzed within a framework of different one-electron band energy approaches. Manifestation of the LSNC nonlinear optical (NLO) properties will be presented separately. It is clearly demonstrated that appropriate choice of LSNC geometry parameters together with proper modification of chemical composition could enhance the key NLO parameters.

Keywords— nanocrystallites, nonlinear optics.

1. Introduction

A new direction in the nanotechnology is intensively developed today, based on possibility of using semiconducting nanocrystallites as materials for optics and electronics, particularly quantum electronics, due to nano-confined size-dependent electronic and optical properties of these nanoparticles [1, 2]. The material attracts interest due to both immediate applications in electronics and communications [3–6] and fundamental science, due to specific properties of such materials [7, 8]. Their applications are based on a quantum confinement influence on material properties, which implies their grain size and shape topology dependence to the corresponding susceptibilities. Traditional nano-confined effects are usually observed for particle size below 8–10 nm [9], where effects of nano-quantization are observed. In such cases, k-space bulk-like dispersion disappears and discrete excitonic-like nano-levels occur inside the energy gap [10].

There exist also an intermediate semiconducting crystallites possessing averaged sizes equal to about 10–50 nm. In this case a coexistence of typical bulk-like properties (first of all possessing energy k-dispersion due to translation symmetry) disturbed by thin near-surface boundary interfaces with thickness about 1.5–4.5 nm is observed. Such properties can be useful for different applications, particularly for biological ones [11], light emitting devices [12], solar cells, laser modulators and deflectors [13], etc.

2. Principal parameters of large-sized nanocrystallites

The quantum-confined boundary interfaces possessing bulk-like as well as dot-like quantized excitonic properties can also be of importance for different experimental utilization of optical phenomena, particularly in nonlinear optics (NLO) due to large charge density gradients determining large values of NLO susceptibilities [14]. Reconstructed interface boundary sheets with thickness of 1.5–4 nm, separating the bulk-like crystallites and surrounding amorphous-like or disordered background, determine these features. Very often this fact is neglected, which precludes appropriate use of their properties.

Principal parameter for the large-sized nanocrystalline (LSNC) is a ratio between thickness of the reconstructed boundary layer (sheet) and total effective diameter of the nanoparticle. Coexistence of bulk-like long-range ordering possessing k-space dispersion, high effective mass, low carrier mobility gradients and quantum size-confined layers possessing a blue spectral shift, gives a rare possibility to operate by principal electron parameters within the same material.

The ZnO and ZnS-based LSNC appear to be particularly appropriate for modelling of luminescent behaviour, exhibiting green and yellow luminescence. Moreover, ZnO LSNC is technologically complementary to GaN, which opens a way for optoelectronics applications. The investigated ZnO-based LSNC were synthesized using different techniques (mechanical crushing, RF sputtering, spray pyrolysis, etc.). This LSNC had grain size of 15–60 nm. The topological profile of the LSNC was prevailingly ovalloid-like. The ZnO-based LSNC were incorporated into polymethyl methacrylate (PMMA) matrices, with LSNC content of 2–6% by weight. Photoluminescent measurements were performed using nitrogen laser excitation ($\lambda = 337$ nm) and grating monochromator with spectral resolution of about 7 nm/mm.

In the present work we introduce a new approach to search for and design of new optoelectronic and non-electronic materials based on LSNC. This approach takes into account both bulk-like and interface contribution; influence of the long-range ordering and influence of the surrounding matrices.

For the luminescent measurements ZnO-based LSNC having sizes of 15–30 nm and reconstructed sheets with thick-

ness of 1–4 nm were used. One can operate by principal nanoparameters by varying the ratio between the LSNC and sheet sizes. Of particular importance is the behaviour of trapping levels caused by the LSNC. Because the LSNC possess prevailingly ovalloid form, one can assume that the LSNC, like spherolites, possess effective sizes corresponding to the sphere with effective averaged renormalized radius. One can introduce an effective coefficient of nanocrystallinity by labelling the effective radius of the LSNC by R and the thickness of the reconstructed sheet by d [3]:

$$Eff_{NC} = \left(R^2/(2Rd - d^2) - 1\right)^{-1}. \qquad (1)$$

3. Luminescent features

Typical measured photoluminescence spectra of ZnO-based LSNC with different structural parameters are shown in Fig. 1; existence of two principal spectral bands of luminescence can be deduced. The first one – originating from bulk-like states (at energy about 3.2 eV), is spectrally stable with respect to the LSNC sizes. For the nano-confined effects the second band covering low-energy wide spectral range at 2.2–2.4 eV is more important. It demonstrates a clear blue shift with increasing thickness of the reconstructed surface region. At the same time, intensities of the main spectral maxima decrease with decreasing sheet thickness t. Generally, this effect may be explained by transfer of excitation between the localized nano-confined reconstructed layers and quasi-continuous bulk-like crystalline states.
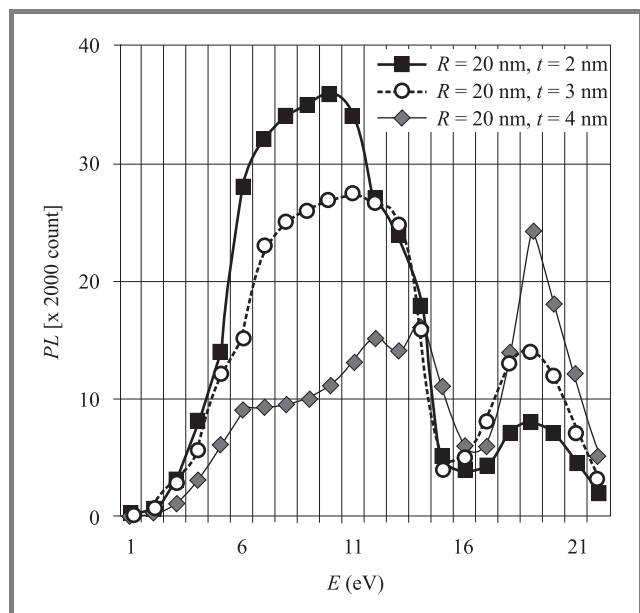

Fig. 1. Photoluminescence spectra of ZnO-based NC incorporated into amorphous-like ZnO matrix, with the different size parameters.

To clarify role played by parameter Eff_{NC}, Fig. 2 shows dependences of the low-energy maxima's spectral positions together with relative intensities of luminescent spectra versus the parameter Eff_{NC} calculated according to Eq. (1). For convenience, the wide spectral band may be divided into separate spectral regions related to different groups of nanoparticles. Another interesting fact is a presence of the near-surface recombination in LSNC determining the distance at which carriers can diffuse to the interfaces before their recombination. With decreasing sizes of the LSNC contribution of the defect states will decrease.
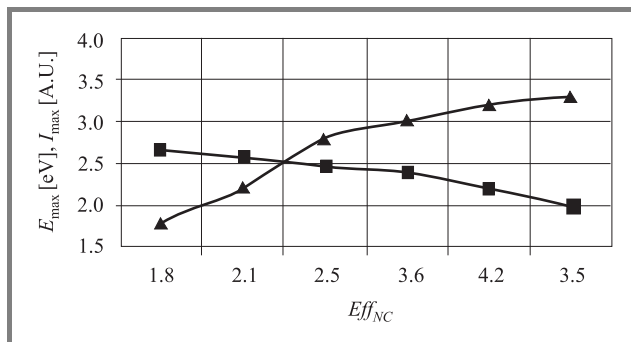

Fig. 2. Dependence of the low-energy photoluminescence spectral maxima (squares) and its relative intensities (triangles) on Eff_{NC}.

This report presents several examples of striking LSNC features and demonstrating key differences between LSNC nanochromophores and other types of nanomaterials – nanowires, dots or crystallites. However, main physical insights clearly indicate substantially different states, compared to nanomaterials studied earlier. This allows to evaluate suitability of LSNC for applications in optoelectronics.
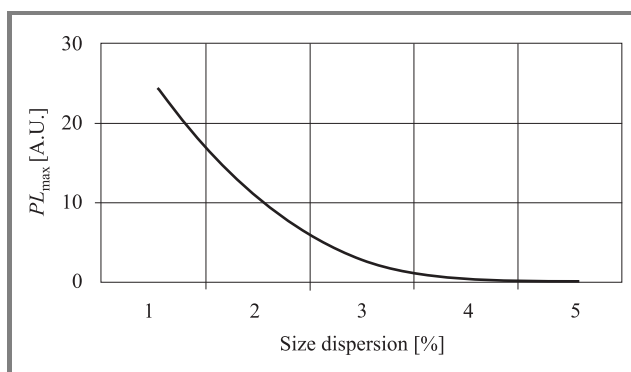

Fig. 3. Dependence of the photoluminescent (*PL*) maxima for the low-energy luminescence of the ZnO-based NC on size dispersion, defined as a ratio of average deviation of NC sizes to total thickness of reconstructed sheet.

Size dispersion also may be crucial for such effects – see Fig. 3. Usually this factor is neglected, which leads to appearance of substantially different results. Recent work performed on high quality ITO nanocrystallites has confirmed this assumption [14].

4. Manifestation of the LSNC in the FT-Raman spectra

The role of the phonon sub-system in nano-confined effects is not clear. This is a consequence of long range manifestation for such kind of states contrary to localized nano-confined effects. For this reason, the Fourier-transform (FT)-Raman spectra were investigated separately for semi-conducting nanocrystallites, particularly for ZnS (Fig. 4) and LSNC incorporated into polymer matrices (Fig. 5).
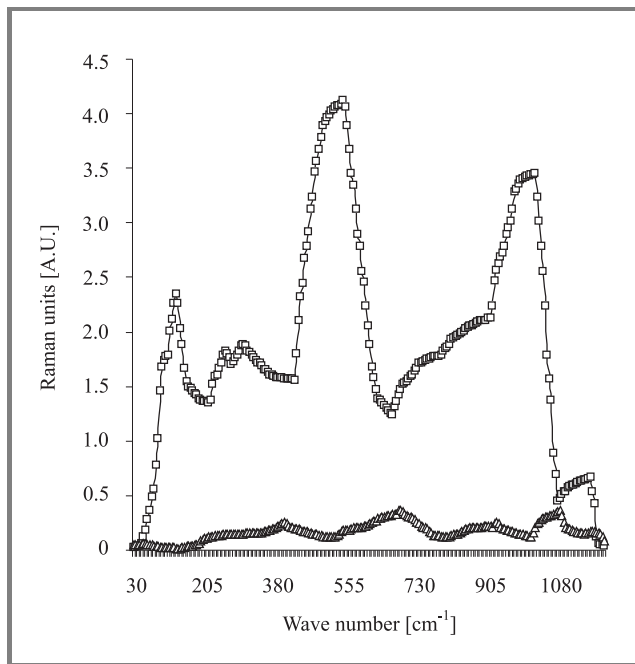
Fig. 4. FT-Raman scattering spectra for the ZnS-based large-sized NC (about 20 nm in diameter). A spectrum for the PMMA is given for comparison (lover curve). Estimated interface sheet thickness is about 2 nm.
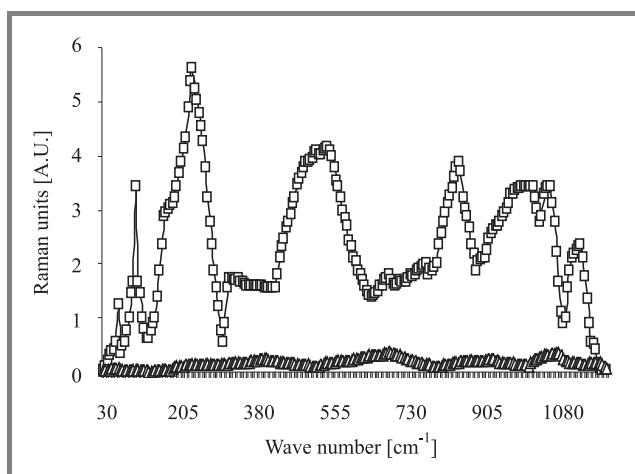
Fig. 5. FT-Raman scattering spectra for the ZnS incorporated into PMMA matrix. The parameters of the LSNC are the same as in the previous case. The PMMA spectrum is presented below for comparison.

Comparing these results with data obtained for the polymer matrices one should emphasize role of the reconstructed interfaces on the effects observed. This observation for different semiconducting nanocrystallites may be considered an additional confirmation that contrary to the traditional nanocrystallites, in case of the LSNC we deal with substantial influence of delocalized bulk phonon sub-system.

5. Band energy approach for research and design of LSNC with desired optoelectronic and nonlinear optical properties

The reconstructed surfaces in LSNC may substantially affect its optical properties, in particular optical nonlinearity, with LSNC having substantial advantages over traditional bulk-like or classical materials in this respect. This is caused by a coexistence of more delocalised band energy-like structural fragments and flat-like localized levels, originating from nano-confined states. The latter are formed exclusively in thin nanosheets separating the LSNC and surrounding material. Most of the published investigations are empirical and there is no systematic study of interfaces using the first principle theoretical methods. However, to use LSNC as material for optoelectronics, data on the state and transitions dipole moments, inter-level energies and related hyperpolarizabilities are needed. A novel situation compared to traditional case is the coexistence of delocalized and localized states, which restrains a possibility of application of the same basis, e.g., plane wave basis set.
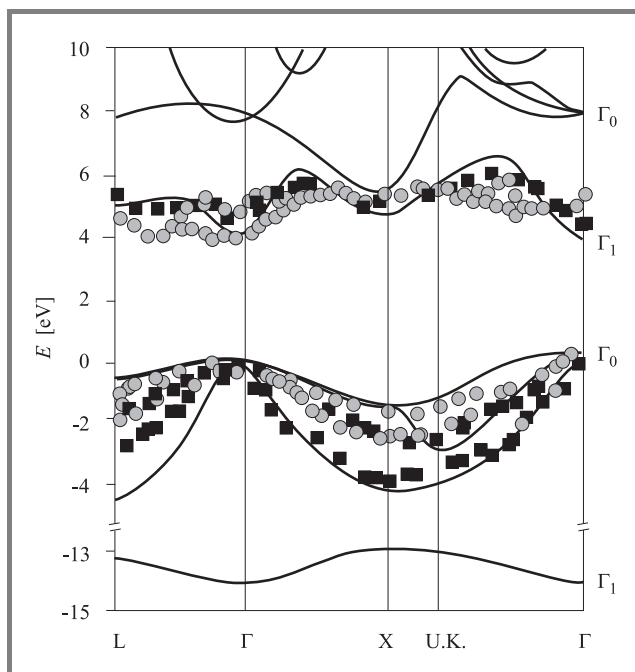
The issue of reconstructed surfaces in the LSNC materials results in complicated application of principles of equilibrium thermodynamics, because such structures are very sensitive to nonequilibrium technological conditions. Unfortunately, several crucial parameters are difficult to be monitored; therefore building a reliable theoretical band energy picture is one of the main goals of this work.

Generally one can expect appearance of reconstructed near-surface structure possessing structural conformations corresponding to thermodynamically metastable (or even unstable) phases. Usually, the classical mechanics molecular dynamics method includes variation of principal structural parameters (bond lengths, angles, torsion angles, etc.) to find a structural configuration corresponding to a minimum of total energy. For the LSNC, we deal with the bulk-like perfect crystallites to which one can apply principles of long-range ordered symmetry and different one-electron band energy methods. However, the long-range ordering usually is broken in the interface region, contrary to perfect bulk-like crystals. In the present work we develop an approach introduced in [10], where an effective complex approach was proposed, combining principles of equilibrium thermodynamics with nonequilibrium perturbation created by surrounding disordered background. The method may be applicable to semiconductors and dielectrics with en-

ergy gaps larger than 1 eV and includes coexistence of many structural fragments (up to 120), renormalized by appropriate weighting factors. The main principle of such approach consists of formation of several coordinated layers (of thickness not more than 6 nm) possessing perfect long-range ordered translation symmetry. Afterwards, we add step-by-step 2–3 structurally disordered layers on the borders of crystalline layers. Geometry optimization is performed between the long-range ordered crystalline layer and disordered layers, assuming fixed atomic positions for crystalline layers.

Such coexistence of localized and delocalised states favours enhanced space gradients of the dipole moments, which determine large optical susceptibilities, being least an order of magnitude larger than in traditional bulk-like or classical nanomaterials. Despite a relatively low volume of such states we are able to achieve the large nonlinear optical susceptibilities. So a main direction of research is finding optimal parameters, like thickness of interfaces, degree of crystallinity of the interfaces, concentration of the LSNC, difference between the energy gaps and dipole moments of the LSNC chromophore and corresponding matrices. To solve this problem only the band energy approach may be useful.

The evaluation of structural form-factor is done following a procedure of superposition of the different structural phases with appropriate weighting factors [10]. As an example one can present ZnS-based LSNC interface phases at distances 1–3 nm from the border separating nanocrystalline and disordered phases (Fig. 6). One can see substantial flattering of the principal bands originating from the layers situated 1–3 nm away from the interfaces. This band dispersion flattering leads to occurrence of electron states possessing substantially different effective masses. Gradients of such effective masses are very large; his favours enhanced hyperpolarizabilities and corresponding nonlinear optical susceptibilities.

Observed enhancement of susceptibilities is due to reconstructed surfaces, which are similar to sheets to which an approach of quantum well effects may be applicable. For narrow wells where with the well widths is less than 3D exciton Bohr radius, excitonic (hole-electron Coulombic interactions) effects dominate electro-optic properties, manifesting through the dipole momentums.

For example, Fig. 7 is a sketch of LSNC interfaces demonstrating the role of the nano-confined and trapping levels. When the thickness of layers is larger, quantum size effects become less important and long-range ordered phonon states seem to be more important. One can clearly see that in the same effective point of the space we have coexistence of several structural fragments. Technologically changes of the corresponding band energy parameters may be performed by monodispersion of LSNC sizes and their concentration. Another way is to find appropriate matrices to enhance the desired dipole moments and related susceptibilities.
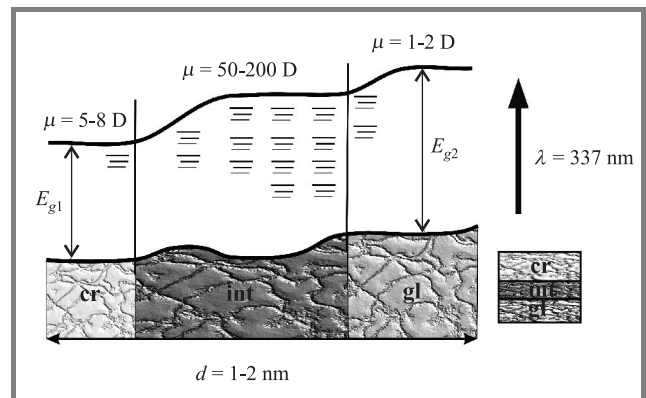
Fig. 7. Principal scheme of interfaces between nano-confined and trapping levels separating polymer matrix and crystalline semiconducting films.

The origin of the observed low-energy luminescence is closely associated with the trapping levels originating from near-surface states in the LSNC (see Fig. 6). With decreasing reconstructed surface-related volume we can suppress intensity of the output luminescent quantum efficiency. The latter play both diagnostic as well as the application role during changes of the effective charge transfer.

The behaviour presented in the previous pictures indicates a substantial difference between LSNC and traditional nanoparticles. Another important aspect substantially attributed to LSNC is an occurrence of oriented spin-polarized vacancy states in the near-surface surrounding polymer sheets. The latter create additional effective layers involved in the process.


Fig. 6. Band energy structure of the ZnS-based LSNC with effective average sizes about 22 nm and film thickness sheet 2.3 nm. The calculations are done for distances 1.2 nm (circles) and 2 nm (squares) from the boundary interfaces.

The quantum efficiency of the *PL* is substantially sensitive to the type of the matrix or more precisely to the dipole momentums of the surrounding polymer matrices. This is substantially different compared to traditional nanocrystallites, where influence of the matrix on the intensity of luminescence is very low due to screening of local Lorenz field effects.

Using the data obtained, one can conclude that the deep-level core luminescence is substantially suppressed by near-surface trapping level luminescence. This fact may serve as an additional confirmation of important role played by near-surface states in the effect observed, contrary to pure nano-confined states in case of traditional nanoparticles. We probably deal with changes originating from both parts of the boundaries – from the polymer boundary states and from the reconstructed crystalline states (Figs. 4 and 5).

It was also revealed, that less polarized matrices (with lower dipole momentums) exhibit substantially less quenching
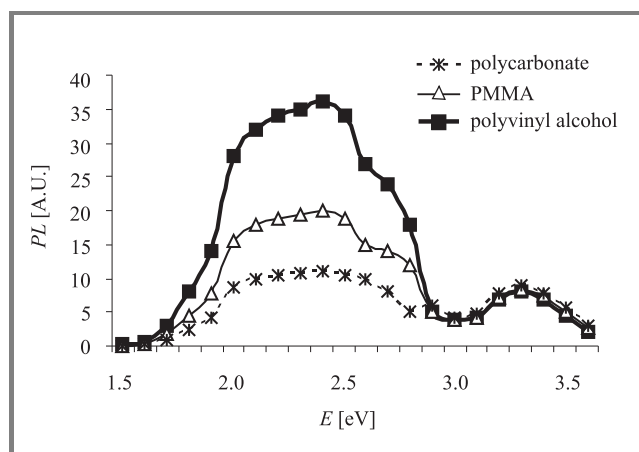

Fig. 8. Dependence of the ZnO-based LSCN *PL* in different host polymer matrix.

of the emission. One can use external cladding for operation by emission in different LSNC (Fig. 8).

6. Origin of nonlinear optical effects formed by the LSNC

Coexistence of localised and delocalised states is a main source of the observed giant optical susceptibilities. However, to utilize these large susceptibilities it is necessary to have an appropriate architecture of particular LSNC chromophore. The nonlinear optical effects used in the optoelectronic devices are of two types. The first of them is a second-order one described by third rank polar tensors and corresponding to linear Pockels effect, optical second harmonic generation. The other is a third-order optical device determining the two-photon absorption and third harmonic generation. Principal difference between the two effects consists in a requirement of the macroscopic non-centrosymmetry for the first class of the devices.

Out of a large number of nonlinear optical effects for such kinds of LSNC, here is presented only a dependence of the two-photon absorption (TPA) for several oxide-based LSNC (see Fig. 9). Figure 9 shows typical dependences of the TPA for the LSNC of different crystalline materials. For comparison, we have shown data for β-BaB_2O_4 and $KTiOPO_4$ LSNC. One can clearly see substantially better parameters of YAB borates (even with different Cr^{3+} content) compared to other materials, which indicate an important role of the LSNC content, contributing to the NLO susceptibilities.
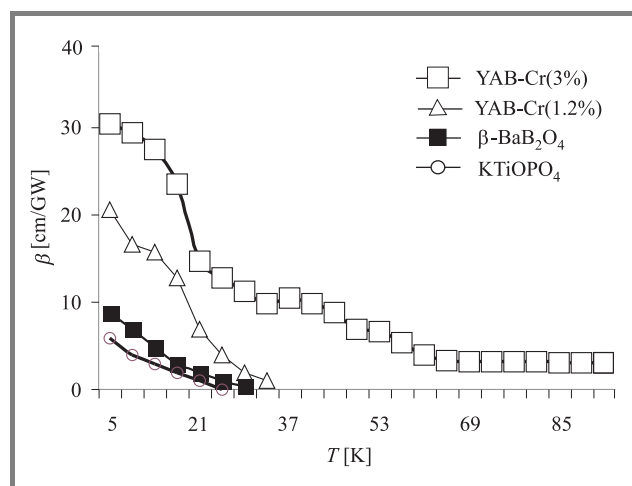

Fig. 9. Temperature dependence of the TPA for the 22–25 nm NC.

The LSNC effect is enhanced at low temperatures, which confirms the crucial influence of the phonon bulk-like subsystem. Moreover, the effects related to condensation of the so-called soft phonon modes responsible for the different kind of phase transformations role begin to play a substantial role at low temperatures. Simultaneously, the localized energy terms of the rare earths give additional contribution to the nano-confined states. Similar behaviours were observed for both second- as well as for the third-order nonlinear optical effects and may serve as an independent confirmation of the applicability of these materials simultaneously as light emitting materials and materials for optical limiters, modulators and for optical parametric transformations.

The effects observed allow to propose LSNC as promising materials for modulation of light, particularly for transmission of information over optical fibres. Their main advantage is large optical susceptibility in comparison to traditional materials. Another option is the possibility of changes of principal parameters like signal to noise ratio by varying their concentration and sizes. By appropriately selecting the host polymer, glass or amorphous-like matrices one can optimise parameters like optical windows [15, 16]. Simultaneous blue-shifted luminescence in the LSNC in combination with large nonlinear optical susceptibilities may be useful for making light emitting diodes, optically operated multi-functional optoelectronic devices, photode-

tectors, etc. Of particular interest is the possibility of photo-induced changes of the basic nonlinear optical parameters, which allows use of the same materials for multiple (erasable) optical recording of information.

7. Conclusions

A principal difference between large-sized semiconducting (dielectric) nanocrystallites and traditional (below 8–10 nm) material is demonstrated, and a parameter for description of the observed effects was introduced. Luminescent, FT-Raman and nonlinear optical spectra demonstrate a crucial role of LSNC interfaces in the observed effects. Following the band structure calculations and molecular dynamics simulations of the interfaces, it is shown that the interfaces are crucial for manifestation of the blue spectral shift and enhanced optical susceptibilities. Another important factor is related to the contribution of the phonon sub-systems, determining high temperature sensitivity of the corresponding effects. Optoelectronic devices having simultaneously efficient light emitting and nonlinear optical properties effectively controlled by LSNC sizes are proposed.

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