The Structure Analysis of Detonation Diamonds Modified Mechanocmecically and Polyethylene/Nano -CdSe (-CdS, -ZnS, -PbS) Modified Nanochemically

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Abstract − The structure of modified nanocrystal materials was studied by comparing experimental diffraction patterns with the pictures simulated according to assumed spatial models. 3D computer modeling nanocrystals (NCs) with the core − shell structure has been here developed. We have shown the XRD analysis is useful in characterizing NC structures including establishing chemical bonding between the core and shell.

1. Introduction

Nanoscale state is characterized by that monitoring crystallite size makes possible obtaining nanoparticle properties differ markedly from the corresponding bulk materials. In some cases, the role played by particle size is comparable to particle chemical composition. In this connection, nanoparticles are extremely important materials in different areas ranging from nanotechnology, non-linear optics, diode lasers, smart sensors, markers in drags, gene sequences to catalysis. Size and even shape selected nanocrystals are ideal building blocks for two- and three-dimensional cluster self-assembled superlattice structures [1]. Semiconductor nanoparticles, such as CdS, CdSe, ZnS, PbS etc., stabilized by protective organic layer are a new form of materials with fundamental interests and technological importance [2, 3]. II−VI semiconductor (especially Cd, Zn (S, Se) and a relatively less studied PbS) NCs are one of the most known classes of quantum dot systems [4]. CdS NCs connecting to biological materials can be used as fluorescent labels [5].

The main goal of our work is to show the possibilities of the structural analysis for characterizing nanoscale materials including those modified by chemical and physical treatment. X-ray diffraction (XRD) is a unique method collected direct structural data on substances under study. Nanocrystals of Cd, Zn, Pb chalcogenides stabilized with o-polyethylene (PE) [2] and detonation nanodiamonds (DND) [6] have been the subject of this investigation. Synchrotron XRD measurements were carried out using a high-resolution triple-crystal θ-2θ diffractometer (λ=1.5406 A). The NC structure was studied using first principles technique involving the comparison between experimental and simulated diffraction patterns.

2. Diffraction pattern calculation

Interference part of the diffraction picture of nanocrystal was computed using atomic coordinates and the Debye (1915) formula [7] for the scattering from a system of independent particles with interatomic distances r_{ij}:

$$I(s) = \sum_{i}^{N} \sum_{j}^{N} f_i(s) f_j(s) \sin sr_{ij} / sr_{ij} =$$
$$= \sum_{i=j}^{N} f_i^2(s) + 2 \sum_{i \neq j}^{N} f_i(s) f_j(s) \sin sr_{ij} / sr_{ij};$$
$$i(s) = \sum_{i \neq j}^{N} f_i(s) f_j(s) \sin sr_{ij} / sr_{ij}. \qquad (1)$$

Here, $I(s)$ is the diffraction pattern consisting of the diffraction on atoms in gaseous state, $f_i^2(s)$, and the interference contribution, $i(s)$; $f(s)$ is the tabulated atomic scattering factor; $s=(4\pi/\lambda)\sin\theta$, A^{-1}, θ is the diffraction angle. To develop structure models of different poly- and nanocrystals (PC and NC), we computed atomic coordinates in three dimensions using known positional and unit cell parameters of polycrystalline state: atomic coordinates, space groups and atomic radii. The radii were required to compute the parameters of coordination spheres (CSs) relative to the central atom. Belonging atoms to a certain CS is established in the following way: each preceding atom was circumscribed by a sphere relative to the central atom and, if a subsequent atom was in contact with this sphere, it is considered incorporating into this CS. Otherwise, this subsequent atom is taken belonging to the next in order CS. Spherical NC may be considered as consisting of a core and shell. Magic particles are called those with the same number of atoms in the core and shell.

3. Structure of CdSe NC in polyethylene

Experimental diffraction pattern of CdSe in PE (Fig. 1), along with intensive discrete reflections from PE, shows diffuse contribution typical of NC matter and weak and broadened discrete reflections coinciding in positions with those from known hexagonal PC h-CdSe [8].
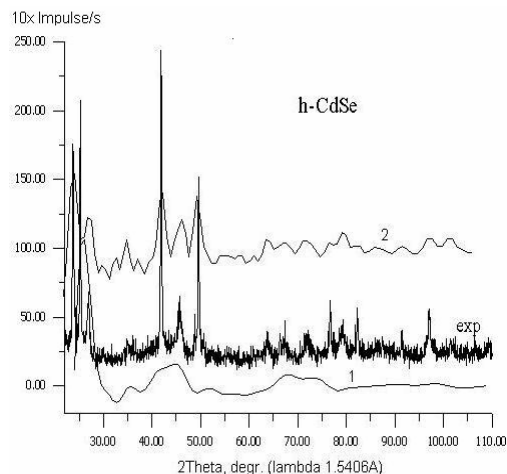

Fig. 1. Experimental pattern of weak and broadened discrete reflections compared to interference contributions calculated from PC h-CdSe: 1 — for 20 atoms in NC, 2 — for nanospheres

The diffraction pattern from PC h-CdSe calculated using the established parameters: a=4.299 A, c=7.01 A (positions of: Cd−2a (0, 0, z; 0, 0, 1/2+z) at z=0; S−2b (1/3, 2/3, z; 2/3, 1/3, 1/2+z) at z=0.375) corresponded in the positions to the experimental discrete peaks of PC CdSe in PE. The best fit between them is achieved for spherical CdSe NCs of r=22.75 A, made up of the 1st to 12th CSs, 1664 atoms, a=4.3, c=7.6 A (Fig.1, curve 2). Experimental pattern of very diffuse discrete reflections was in agreement with that (Fig.1, curve1) calculated for non-spherical NC of (2a×a×2c) size at: a=3.5 A, c=7.6 A, different from the PC parameters. This suggests a difference between the structures of non-spherical NC in PE and spherical NC and PC, in other words, an extension of zigzag-like (Cd-Se-Cd-Se-Cd-) chain in non-spherical NC compared to PC. The interatomic distance r(Cd-Se)=2.85 A was found bigger that for PC, the latter being equal to 2.63 A and close to the known value of 2.65 A [9].

We calculated the patterns for spherical h-CdSe NCs with different ratio between the number of core and shell atoms. Experimental pattern with smoothed discrete reflections fitted well that calculated for spherical NC of (r=22.75 A) size containing 789 atoms in the core made up of the 1st to 9th CSs (r_{co}=17.19 A) (Cd as a central atom) and 875 atoms in the shell made up of the 10th to 12th CSs (Δr_{sh}=22.75−19.43 A). A small difference in the number of core and shell atoms is consistent with a

known ability of spherical h-CdSe NCs (r=22 A, 2000 atoms) [10] to withstand pressure 2−3 times greater than pressure in case of CdSe PC.

4. The structure of NC CdS in polyethylene

Experimental diffraction pattern of CdS in PE (Fig. 2, curve 1) comprises an additive sum of patterns of PE, PC h-CdS (space group N186, a=4.14092, c=6.7192 A [11]) and NC h-CdS (of (1a×2a×2c) size, space group N186, established parameters: a=4.14092, c=7.5 A).
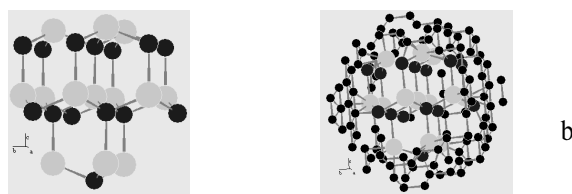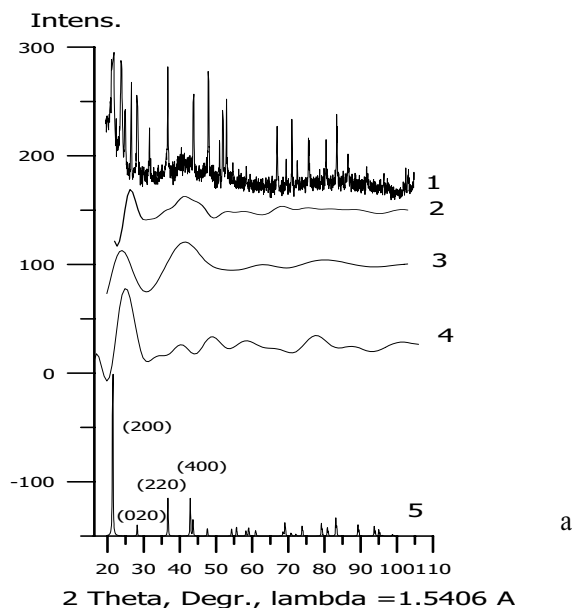

Fig. 2. a: 1 — experimental diffraction pattern of nano-CdS in PE shows the discrete PE reflections, PC h-CdS and greatly diffusive reflections. Greatly diffuse NC patterns calculated for: 2 — h-CdS of (1a×2b×2c) size; 3 — h-CdS core (left model in Fig.: Cd atoms — light circles, S and C — dark circles of different size); 4 — spherical NC h-CdS/PE consisting of h-CdS core and PE shell (right model in Fig.). 5 — polycrystalline PE. b: model — a spherical NC h-CdS/PE consisting of h-CdS core (a=4.14092 A, c=7.5 A, space group N186, r=5 A: the 1st CS (4 S atoms); the 2nd CS (12 Cd, 10 S atoms) and PE shell (r=6.75−7.55 A, the 6th CS (51 atoms), the 7th CS (56 atoms)

Comparison between experimental pattern of PC CdS in PE and calculated pictures of PC h-CdS (Fig. 2, curves 2−4) shows close agreement between discrete peak positions in the patterns. A detailed fit was achieved by varying atomic positions and z valu-

es and the best results were obtained with $2a$ $(0,0,z; 0,0,1/2+z)$; $2b$ $(1/3,2/3,1/2+0.375)$. According to (1), reflection positions depend on the values of interatomic distances in spatial structure. Simulation of the features (the positions of greatly smoothed discrete reflections) of patterns allows establishing a size of h-CdS NCs, dependent on amount of interatomic distances of various lengths in supposed spatial model. In case of NC h-CdS in PE, the position of a head experimental reflection fitted that calculated for a spherical NC h-CdS consisting of two CSs with respect to the centre Cd atom. The experimental NC diffuse reflections (Fig. 2, curve 1) correspond in the positions to groups of discrete PC reflections. It points to a similar short-range order of NC and PC states. Calculation of diffraction patterns was performed for molecular formations consisting of one, two, three h-CdS unit-cells. Fig. 2 shows agreement (in short-range order at $2\theta\approx40°$) between the positions of experimental and simulated reflections in case of diffracting independently of one another molecular species consisting both of two h-CdS unit-cells arranged along the z axis and of spherical particles formed by two CSs. Preference is given to spherical NCs because of fit of a head reflection ($2\theta\approx25°$) a group of (100, 002, 101) h-CdS reflections. The order of atomic arrangement in NC unit-cell along z axis was noticeably different from that in PC. According to a short-range ordering, interatomic distance, r(Cd-S)=2.5 A, equals to a sum of covalent radii of r_{Cd}=1.48 A and r_S=1.04 A [9].

5. The structure of NC ZnS in polyethylene

Experimental diffraction pattern of ZnS in PE (Fig. 3) shows weak diffuse reflections from NC considered as the traces of discrete PC reflections. These traces are due to a group of crystallographic NC planes whose size is comparable to a wavelength of diffracting radiation. When the positions of trace reflections are compared to those in the calculated pattern (Fig. 3), it is apparent their good consistency with the peak positions of polycrystalline hexagonal h-ZnS. So, observing smoothed discrete reflections at the discrete peak positions of PC suggests the presence of NC h-ZnS.

Modeling interference diffraction component responsible for a spatial atomic arrangement was performed for h-ZnS NCs of diverse shape and size (space group N186, a=3.82098 A, c=6.2573 A, $2b$: (1/3, 2/3, 0; 1/3, 2/3, 0.375)) [12]) (Fig. 3). A comparison of the reflections positions and character of the simulated interference contributions with experimental those revealed their accordance with spherical NC of 17.96 A size (ionic radius of Zn) rather than with those of 16.27 A size (covalent radius of Zn). A realization of NC with ionic Zn radius is supported by appearing additional reflections (marked *) lacking in PC h-ZnS and responsible for diffrac-

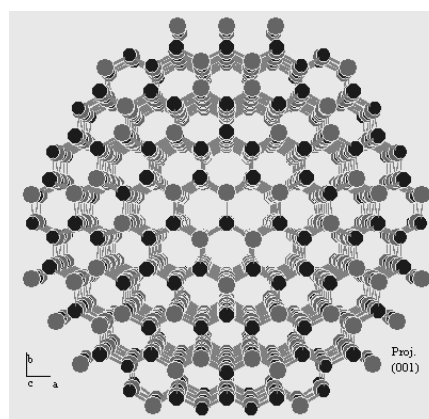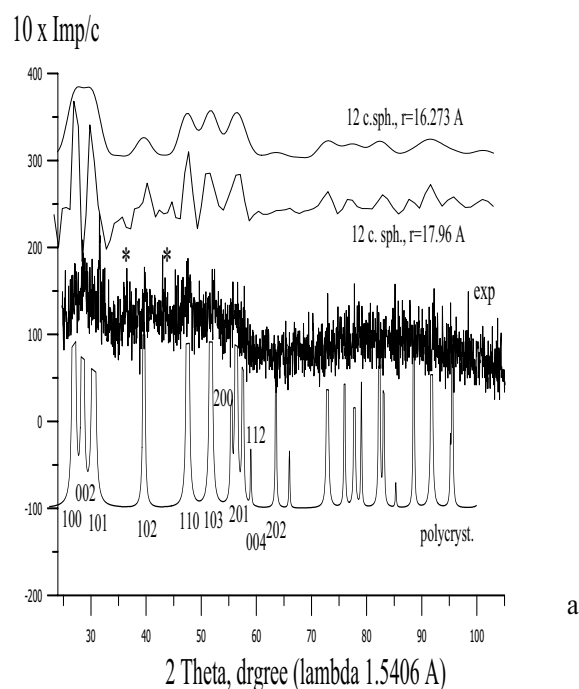tion on electronic density distribution in NC other than in PC.

Fig. 3. *a*: Experimental diffraction pattern compared to simulated those from ZnS/PE for: hexagonal PC h-ZnS (polycryst.); spherical NC of size 17.96 A (with ionic radius) and size of 16.27 A (with covalent radius). The reflections labeled * are absent in PC h-ZnS. *b*: shows 3D structure model of spherical NC made up of 17 CSs (spherical and non-spherical contour was observed depending on CS size)

6. The structure of NC PbS in polyethylene

Experimental diffraction pattern of PbS in PE (Fig. 4, curve 1) consists of the patterns of PC PE, cubic PC c-PbS (space group N225, a=5.9362 A, atomic positions: $4a$ (0, 0, 0), $4b$ (0.5, 0.5, 0.5)) [13] and NC c-PbS of ($8a\times a\times a$) size at lattice parameter a=5 A. The positions of experimental discrete PC PbS reflections are in agreement with known reflections of PC c-PbS.
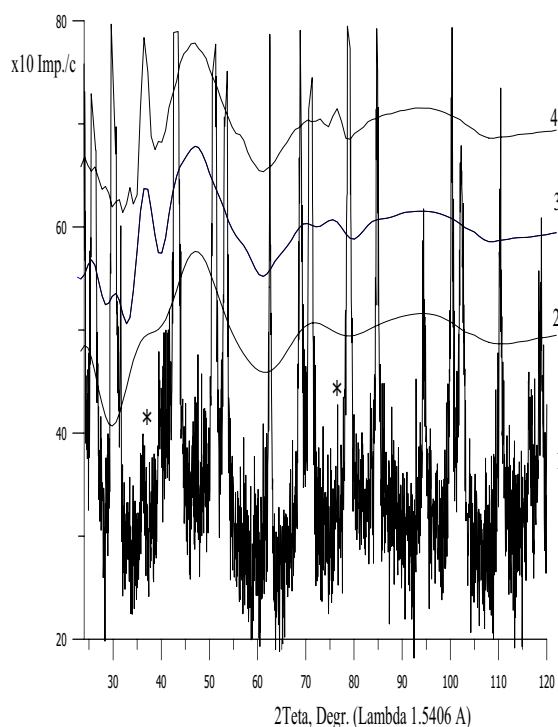
Fig. 4. Experimental diffuse part (1) of c-PbS inPE compared to a calculated interference contribution from NC c-PbS at a=5A for: 2 − two ($2a \times a \times a$); 3 − four ($4a \times a \times a$); 4 − eight ($8a \times a \times a$) unit cells. Discrete reflections are seen from PC c-PbS

Simulated diffuse reflections (Fig. 4, curves 2−4) from NC c-PbS correspond in their positions to groups of the discrete (220; 311; 222; 331;420;422; 333) reflections of PC c-PbS as well as to diffuse reflections in experimental diffraction pattern. It is an evidence for nanocrystalline nature of c-PbS in PE and similar short-range order parameters of NC and PC. In our case, for NC, besides diffuse reflections in positions of associated discrete PC peaks we have observed additional experimental reflections at $2\theta \cong 32$ and 77° (Fig. 4, labeled *) absent in PC. Increasing NC size in range of ($2a \times a \times a$) to ($8a \times a \times a$) results in noticeable sharpening of additional reflections in the calculated patterns that become similar to the experimental pattern of needles of ($8a \times a \times a$) size. Additional experimental reflections in NC c-PbS typical of the crystallographic planes are due both to a different distribution of the electronic density in NC and PC and effective pair interatomic interactions.

It has been known that on grinding crystals into fragments of lesser size the properties of small particles of single crystal remain unchanged. In this connection, at first sight, it is not evident that the properties of crystal changed when passing from crystal of micron size (polycrystalline state) to nanocrystals. Note that each atom in condensed state has, within its short-range order structure, the atoms localized within potential pit. In case of liquid Pb (in absent of long-range ordering) oscillating long-range interaction has repulsive region at r=5.3−6.3 A [14], outside of a basic minimum (r=4.95 A). As a result, Pb atoms in NC PbS are surrounded by S atoms at the nearest interatomic distances at $a/2$=2.97 A (a=5.9362 A, the PbS lattice parameter), between Pb atoms. Appearing the additional experimental reflections (labeled * in Fig. 4) suggests an existence of repulsive region around S atoms at the established distances responsible for a period $d \cong 2.72$ A in NC c-PbS lattice. Scattering matter (covalent fraction of chemical bond) in repulsive potential region accounts for an additional reflection. So, in case of NC ($8a \times a \times a$) c-PbS, unlike PC c-PbS, a part of electronic density on Pb atoms via electronic bridge occurs between Pb and S atoms. In NC c-PbS, the crystallographic planes (200), (220) are occupied with atoms while the (330) plane is related to electronic density between Pb and S atoms.

7. Detonation nanodiamonds

Detonation nanodiamonds (DND) represent solidified drops of liquid carbon produced under high pressure [6]. Such DNDs compared to diamonds of static and impact synthesis show unique properties due to their high dispersion and large amounts of surface carbon atoms. As a result, a high degree of crystal lattice distortion of DND may be suggested and revealed. However, these assumptions need the experimental support. X-ray analysis using a comparison between experimental diffraction patterns and those simulated on the basis of successive modeling spatial structure with use of reflection positions provide a useful check on these assumptions. After mechano-chemical treatment, DND powder show an additional diffraction reflection between (220) and (311) known diamond peaks (Fig. 5, marked *). Our earlier attempt [6] to simulate diffraction pattern using model of diamond crystal lattice allowed qualitative reproducing this unusual experimental pattern and revealed difference between nanosized and polycrystalline diamonds. DNDs were considered as consisting of a core and two shells. The reflections positions (hkl) in calculated DND pattern depend on size, shape, unit-cell parameters of diamond according to (1). Now, to achieve the closest approach between experimental and simulated patterns we varied a degree of compression of a parameter in the core. Assuming a compressed a parameter by 5% ($a \approx 3.3884$ A), we obtained a consistence between experimental and calculated (111) positions. According to the atomic coordinates, the core made up of 12 coordination spheres (CSs} was of r=12.2 A size. Note the 12th CS in the deformed and normal lattices has the close parameters, suggesting formation of intergace. Lowering a compression from 2.5−1.25 % to a normal crystal lattice (modeling the transition region made up of the 7th to the 12th

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CSs) gives no agreement between the shape and positions of other reflections in experimental and simulated patterns. The best result was obtained in case of a compressed first (by 2.5 %) and non-compressed second shells surrounding the core. The first shell was of r=13.11−16.4 A and included the 13th to the 18th CSs, the second has r=17.29 A and involves only 19th CS, in which ≈15 % atoms were accidentally missing (the outer shell being loosely formed) relative to amount of atoms in an analogous CS in natural diamond. Reproducing two experimental weak additional reflections (2θ≈63−66°) gives cause for revealing a new allotropic form of diamond.
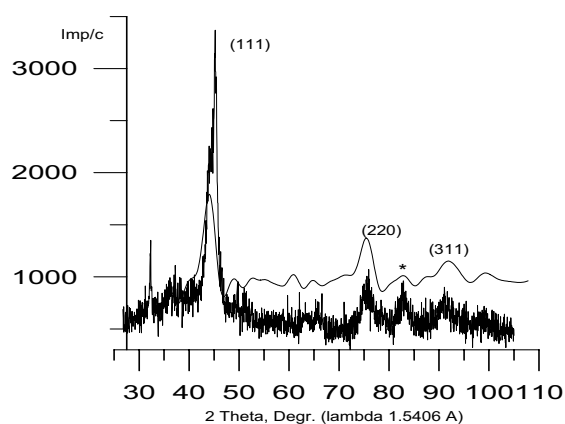

Fig. 5. Experimental (1) and calculated (2) diffraction patterns of detonation diamond. The reflection labeled * are absent in natural diamond

8. Conclusion

It has been shown that XRD analysis can be used for characterizing nanocrystals and monitoring the particle size that is essential for employing them as molecular formations in nanotechnology. Knowledge of difference between NC and PC patterns is important for the nanochemistry of the condensed matter and for the progress in solid state chemistry.

NC h-CdSe in PE are defined as spherical (r=22.75 A) particles forming no interface between h-CdSe core and PE shell. NC h-CdS in PE (r=5 A) and h-ZnS (r=17.96 A) are also established as spherical particles. According to interatomic distances, NC h-Zn-S corresponds to particles with ionic chemical bond. The lattice parameters of NC h-CdS and c-PbS are found different from those for PC state. NC c-PbS was of non-spherical shape with covalent fraction in chemical bond. According to difference between diffraction of NC and PC (at invari-

able atomic coordinates), NC c-PbS was characterized as molecular formations (lack of long-range ordering) but not a phase. The PE lattice parameters and conditions of synthesis have influence on NC size. It has been established that DND treated mechano-chemically were of spherical shape and had a compressed core in the absence of extensive interface between the core and shell. NCs size and shape have been found not from a width of diffraction reflections but using their spatial structure model involving the atomic coordinates. Computer simulation of hollow spherical NCs was performed using known crystalline structures and the core-shell model that allows studying not only the inorganic core and organic shell of the composites but also their interface. 3D computer modeling NC core-shell structures has been first carried out.

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