Optical study of ZnP$_2$ nanoparticles in zeolite Na–X

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Abstract

Nanoparticles of the II–V semiconductor (ZnP$_2$) were prepared and investigated. ZnP$_2$ nanoparticles were incorporated into zeolite Na–X matrix. Absorption, diffuse reflection (DR) and photoluminescence (PL) spectra of ZnP$_2$ nanoparticles were measured at the temperature of 77 K. Five bands B$_1$–B$_5$ are observed in both the DR and PL spectra demonstrating the blue shift from the line of free exciton in bulk crystal. We attribute the B$_1$–B$_5$ bands to five stable nanoparticles with size less than the size of zeolite Na–X supercage. We observed Stokes shift of the PL bands with respect to the absorption bands. This dependence of this Stokes shift on the particle size is nonmonotonic.

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1. Introduction

Many different methods have been used for preparation of semiconductor nanoparticles, e.g. preparation of nanoparticles in solutions [1], glasses [2] or polymers [3]. However, it is not easy to control the size distribution of small particles with countable number of atoms in these methods. Matrix method based on the incorporation of materials into the 3D regular system of voids and channels of zeolites crystals could be one of the possible solution [4, 5]. Zeolites are crystalline aluminosilicates with cavities, which size can vary in the range from one to several tensh nanometers. It depends on the type of aluminosilicate framework, ratio Si/Al, origin of ion-exchanged cations, which stabilise negative charge of framework, etc. Zeolite Na–X, which has been used in the present work has Si/Al ratio equal 1, Fd3m symmetry and two types of cages: one is sodalite cage—truncated octahedron with diameter 8 Å and supercage, which is formed by the connection of sodalites in diamond-like structure with the diameter of about 13 Å [6]. All cages are interconnected by shared small windows and arranged regularly. Thus, the cages can be used for preparation of small semiconductor nanoparticles.

Many works have been reported on the nanoparticles of II–VI [1], III–V [7], IV–VI [8], II–VII, IV–VII, V–VII [9] and IV [10] types of semiconductors. But to the best of our knowledge the nanoparticles of II–V type have not been studied yet. The present paper is the first study of ZnP$_2$ particles. Wet chemistry methods are not applicable for a production of ultrasmall ZnP$_2$ particles due to their high reactivity in water. It is hard to expect their stability in glass melt as well. Thus, incorporation into zeolite cages seems to us to be one of the most suitable methods for preparation of ZnP$_2$ nanoparticles.

Quantum confinement of charge carriers in small nanoparticles leads to new effects in optical properties of the nanoparticles. Those are the blue shift of exciton spectral lines originating from the increase of the kinetic energy of
charge carriers and the increase of the oscillator strength per unit volume. These effects are quite remarkable when the size of the nanoparticle is comparable with or smaller than Bohr radius of exciton in bulk crystal. Since the exciton Bohr radius in bulk monoclinic ZnP$_2$ ($\beta$-ZnP$_2$) is quite small (15 Å), the problem to reach the quantum confinement for this material is quite difficult. Therefore, zeolite is the good candidate to solve this problem, as its cages are rather small and can contain only small particles.

Bulk $\beta$-ZnP$_2$ crystal is the direct-gap semiconductor. As this biaxial crystal is strongly anisotropic, its optical spectra are characterised by three exciton series. The lowest energy exciton peak is observed at 1.55913 eV [11]. As the bulk crystal has rather small energy gap (1.6026 eV), the blue shifted exciton lines of ZnP$_2$ nanoparticles are expected to be in the visible spectral region.

2. Technological and experimental procedures

For the preparation of ZnP$_2$ nanoparticles we used crystals of $\beta$-ZnP$_2$ and synthetic zeolite of Na–X type. Zinc diphosphide was of 99.999% purity. The framework of zeolite Na–X consists of sodalite cages and supercages with the inside diameters of 8 and 13 Å, respectively. ZnP$_2$ molecule seems to us to be too large to be incorporated into small sodalite cage, because of the existence of many Na cations. Therefore, it is naturally to assume that only the supercages can be the hosts for ZnP$_2$ nanoparticles. Zeolite and ZnP$_2$ crystal were dehydrated in quartz ampoule in vacuum of about $2 \times 10^{-5}$ mm Hg for 1 h at 400 °C. Then ampoule was sealed. We used 100 mm length ampoule for space separation of ZnP$_2$ source and zeolite in it. ZnP$_2$ was incorporated into the zeolite matrix through the vapour phase at 840 °C in source region and 835 °C in zeolite region for 100 h. The cooling of ampoule was carried out gradually with inverted temperature gradient. An XRD pattern showed that the lattice of zeolite monocrystals was not destroyed at mentioned temperatures, i.e. the crystallinity of zeolite was retained (see Fig. 1).

The EDX analysis of the substance incorporated into the zeolite matrix was performed. We obtained that incorporated into zeolite matrix substance was ZnP$_2$, and that the loading level of ZnP$_2$ into zeolite was 5 wt%. Samples in quartz ampoule were dipped into liquid nitrogen during the experiment. As a light source for the absorption and diffuse reflection measurements a tungsten–halogen incandescent lamp was used. An Ar$^+$ laser with wavelength 4880 Å was used for the excitation of the luminescence.

3. Results and discussion

Absorption, diffuse reflection (DR) and photoluminescence (PL) spectra of the ZnP$_2$ nanoparticles incorporated into the zeolite Na–X matrix were measured at the temperature of 77 K. The absorption and DR spectra of the studied nanoparticles are presented in Fig. 2. Conventional absorption spectrum was obtained from the transmission one measured from the layer of 0.3 mm thickness of powder of zeolite with ZnP$_2$. The layer of zeolite with ZnP$_2$ is not the homogenous transparent medium. Thus, the light propagation has the character of many acts of reflection and scattering. So, the fine structure blurs and we observe that the absorption coefficient increases monotonically with increase of the photon energy in the range from 1.66 to 2.60 eV. The absorption spectrum can be obtained from the diffuse reflection spectrum by conversion with Kubelka-Munk function $K(h\omega) = \left[1 - R(h\omega)\right]^2/2R(h\omega)$, where $R(h\omega)$ is the diffuse reflectance normalised by unity at the region of no absorption. Obtained spectrum is more interesting than
conventional absorption one as it demonstrates clear structure. Five bands marked as B1–B5 are observed in the spectrum (Fig. 2). The spectral positions of these bands are presented in Table 1. All these bands demonstrate the blue shift (Table 1) from the line of free exciton (1.55913 eV) in the bulk β-ZnP2 crystal. The photoluminescence spectrum (Fig. 3) shows the same structure as the DR spectrum, i.e. PL spectrum consists of the same five B1–B5 bands. Their spectral positions are presented in Table 1. The PL bands demonstrate blue shift from the exciton line in bulk crystal also (Table 1). The observed blue shift allows us to attribute these bands to the electronic transitions in ZnP2 nanoparticles incorporated into zeolite matrix. SEM images of the zeolite crystals with incorporated ZnP2 showed that the formation of large ZnP2 nanoparticles on an external surface of zeolite did not occur. Therefore, one can conclude that the observed B1–B5 bands originate from ZnP2 nanoparticles incorporated into the supercages of zeolite.

It is often observed that nanoparticles with certain number of atoms are characterised by higher binding energy and are more abundant in the sample. This effect is well known for nanoclusters of different types, i.e. for C [12], Ar [13], Na [13], and for the nanoparticles of II–VI semiconductors [14]. The ab initio calculations aimed to find such ZnP2 particles were performed. We have found that such ZnP2 particles exist. Those are (ZnP2)6 and (ZnP2)8 ones (see Fig. 4). The (ZnP2)6 particle is characterised by the binding energy 1.90 eV per atom, and the (ZnP2)8 one—2.12 eV per atom. The maximum size of (ZnP2)6 particle is 8.5 Å, and the maximum size of (ZnP2)8 is 8.7 Å. Most probably, some other stable particles exist as well. Now, we continue the theoretical search of other stable particles. Thus, B1–B3 bands can be attributed to five stable ZnP2 nanoparticles incorporated into the supercages of zeolite matrix. Probably, they are stoichiometric since the EDX analysis shows no evidences of ZnP2 decomposition at the temperature of 840 °C used for its sublimation.

The observed blue shift of the absorption and luminescence bands is the result of the quantum confinement of electrons and holes in ZnP2 particles. The exciton Bohr radius a in bulk crystal is 15 Å that is larger than radius of zeolite supercage (6.5 Å). So, the strong confinement model can be used to consider the quantum confinement of the carriers in nanoparticles. The experimental value of the blue shift obtained from the spectral position of B3 band in DR spectrum is 0.282 eV. In Ref. [15] the finite confining potential was used to calculate blue shift for nanoparticles with strong confinement. However, for experimental blue shift of 0.282 eV the theory gives the value of the particle diameter of about 30 Å that is considerably larger than the diameter of zeolite supercage (13 Å). So, the value of blue shift calculated by the effective mass approximation are substantially different from the experimental one. It means probably that the effective mass approximation fails for considered particles with small number of atoms. Another explanation of the obtained small value of the blue shift is the shift of electron and hole energy levels to the low energy due to the tunnelling between the neighbouring supercages.

As it can be seen from Fig. 2 the intensities of the bands increase with an increase of the respective photon energy in DR spectrum. Meanwhile, the opposite situation takes place for PL spectrum (Fig. 3). Here the intensities of bands increase with the decrease of the energy. This effect can be explained as follows. Lower intensities of the PL bands corresponding to the smaller particles can be explained by reabsorption of their emission by larger particles. The reabsorption is due to overlap of the corresponding bands.
absorption into excited states and phonon-assisted transitions.

One can see from Table 1 that the PL bands have the Stokes shift from the absorption ones. The value of this shift is in the range from 0.078 to 0.135 eV. Such shift is well known both in the molecular spectroscopy and in the spectroscopy of nanoparticles. It is known that this kind of Stokes shift (so-called Frank-Condon shift) is due to vibrational relaxation of the excited molecule or nanoparticle to the ground state. The dependence of Stokes shift in the spectra of ZnP$_2$ particles in zeolite on the size of particle is nonmonotonic. For the smallest particles the increase of the Stokes shift with a decrease of the nanoparticle size is observed. Such dependence can be explained by the theory developed in Ref. [16] where the first-principle calculations of excited-state relaxations in nanoparticles have been performed and the dependence of respective Stokes shift on particle size have been obtained. As it is shown in Ref. [16], for the smallest particles the observed Stokes shift is the Frank-Condon one which is the result of the vibrational relaxation of the particle in the excited electronic state. Meanwhile, for larger particles the opposite dependence is observed, namely the Stokes shift increases with the increase of the particle size.

Fig. 4. Calculated structure of the stable ZnP$_2$ particles: (a) structure of the (ZnP$_2$)$_6$ particle, and (b) structure of the (ZnP$_2$)$_8$ one. Zn atoms—black balls, P atoms—gray balls.

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