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Optical properties and structure of most stable subnanometer $(ZnAs_2)_n$ clusters

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Abstract

$ZnAs_2$ nanoclusters were fabricated by incorporation into pores of zeolite Na–X and by laser ablation. Absorption and photoluminescence spectra of $ZnAs_2$ nanoclusters in zeolite were measured at the temperatures of 4.2, 77 and 293 K. Both absorption and PL spectra consist of two bands which demonstrate the blue shift from the line of free exciton in bulk crystal. We performed the calculations aimed to find the most stable clusters in the size region up to size of the zeolite Na–X supercage. The most stable clusters are $(ZnAs_2)_6$ and $(ZnAs_2)_8$ with binding energies of 7.181 and 8.012 eV per $(ZnAs_2)_1$ formula unit, respectively. Therefore, we attributed two bands observed in absorption and PL spectra to these stable clusters. The measured Raman spectrum of $ZnAs_2$ clusters in zeolite was explained to be originated from $(ZnAs_2)_6$ and $(ZnAs_2)_8$ clusters as well. The PL spectrum of $ZnAs_2$ clusters produced by laser ablation consists of a single band which has been attributed to the emission of $(ZnAs_2)_8$ cluster.

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1. Introduction

Many different methods have been used for fabrication of the semiconductor nanoparticles, e.g. fabrication of nanoparticles in solutions [1], glasses [2] or polymers [3]. However, it is not easy to control the size distribution of small nanoparticles with countable number of atoms (so-called clusters) 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 solutions [4,5]. Moreover, the subnanometer and nanometer clusters are very interesting as they are in the

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intermediate position between the molecules and typical nanocrystals. Usually, the structure of nanoclusters is different from the structure of nanocrystals, which resembles the structure of bulk crystals [6]. As a rule the methods of calculation of the structure of electronic states of nanocrystals, which are based on the effective mass approximation are not applicable for clusters. Thus, nanoclusters are very interesting objects as their structure, electronic and vibrational properties are quite different from the crystalline nanoparticles. Zeolites provide the opportunity to obtain extremely small clusters in the pores with diameters up to 15 Å. Zeolites are crystalline alumosilicates with cavities whose diameter can vary in the range from 7 to 15 Å. It depends on the type of alumosilicate 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 to 1, Fd3m symmetry and two types of cages: one is the 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 [7]. All cages are interconnected by shared small windows and arranged regularly. Thus, the cages can be used for fabrication of small semiconductor nanoclusters.

Laser ablation (LA) is a well-known method to produce nanoclusters by ablating material from a solid target [8]. LA usually is performed in vacuum, or sometimes in inert gas such as argon or more reactive gases such as ammonia or nitrogen. Recently, a new variation of LA has been reported whereby the target is immersed in a liquid medium, and the laser beam is focused through the liquid onto the target surface [9]. As a rule, the nanoclusters formed at the ablation have diameters from several angstroms to several tens of angstroms. LA technique has been used to produce nanoclusters of semiconductors (see e.g. Refs. [10,11]) and metals (see e.g. Ref. [12]).

The nanoclusters of II–V semiconductors are studied rather poorly. To our knowledge there are several works on Cd_3P_2 nanoclusters fabricated by wet chemistry methods [13,14] and by thermolysis [15] and alcoholysis of organometallic species [16]. Also, in our recent work [17] we have reported the fabrication and study of the optical properties of the nanoclusters of another II–V semiconductor (ZnP_2) incorporated into zeolite Na–X matrix. The present paper is the first study of the nanoclusters of another II–V semiconductors: zinc diarsenide ($ZnAs_2$). Wet chemistry methods do not seem to be suitable for the production of ultrasmall II–V nanoclusters due to their high reactivity in water. It is hard to expect their high stability in glass melt as well. Thus, incorporation into zeolite cages and production by laser ablation seem to us to be one of the most suitable methods of fabrication of II–V semiconductor nanoclusters.

Quantum confinement of charge carriers in nanoclusters leads to new effects in their optical properties. They 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 [18,19]. These effects are quite remarkable when the radius of the nanoparticle is comparable with or smaller than the Bohr radius of exciton in bulk crystal. Incorporation into zeolite pores and laser ablation are quite promising methods to produce small nanoclusters in which these effects can be studied.

Bulk $ZnAs_2$ crystal is the direct-gap semiconductor. The symmetry of its lattice is characterised by the space symmetry group C_{2h}^5 (monoclinic syngony). As this biaxial crystal is strongly anisotropic, its optical spectra are characterised by three exciton series. Since the lowest energy exciton peak is observed at 1.0384 eV [20,21], the blue shifted exciton lines of $ZnAs_2$ nanoclusters are expected to be in the visible spectral region.

2. Structure and optical properties of $ZnAs_2$ nanoclusters in zeolite Na–X matrix

For the fabrication of $ZnAs_2$ nanoclusters we used $ZnAs_2$ bulk crystals and synthetic zeolite of Na–X type. The framework of zeolite Na–X consists of sodalite cages and supercages with the inner diameters of 8 and 13 Å, respectively. $ZnAs_2$ nanoclusters probably are too large to be incorporated into small sodalite cage, because of the existence of many Na cations. Therefore, it is