PREPARATION AND PROPERTIES OF COLLOIDAL GaP NANOPARTICLES

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Abstract. *Recent results regarding technological aspect of preparing high quality GaP nanoparticles for use in light emissive devices are presented in this work.*

The nanoparticles have been prepared by a colloidal low temperature method using a new precursor as source of gallium atom such as gallium acetylacetonat and temperature treatment in order to improve the quality of nano-suspension and to characterize their dimensions. Trioctilphosphine oxide (TOPO) was used to avoid coagulation and aggregation of nanoparticles. Photoluminescence and. X-ray diffraction and high resolution transmission microscopy (TEM) of the nanoparticles prepared under different conditions are investigated.

We demonstrate that by using as a sources of gallium atoms of gallium acetylacetonate ($Ga[CH_3COOH=C(O-)CH_3]_3$) uniform fraction of nanoparticles of about 8-10 nm in diameter are produces. These materials show a luminescence maximum at around 3.2 eV determined by quantum-confinement effects.

Keywords: *GaP nanoparticles, colloidal synthesis, photoluminescence spectroscopy.*

I. Introduction

The synthesis of GaP colloidal nanoparticles is important for understanding the fundamental properties of wide indirect-band-gap semiconductor and for developing optoelectronic and light emitting devices operated in the ultraviolet, blue and blue-green spectral rang from 250 to 500 nm [1]. Semiconductor colloidal nanocrystals (NCs) are wet chemically grown nano-objects whose optical and electronic properties are strongly governed by quantum-confinement effects. Several methods such as aqueous synthesis of monodispersed GaP nanocrystals [2], hydrothermal synthesis by the reaction of yellow phosphorus with gallium metal in benzene [3] have been reported to synthesis GaP nanoparticles. In our previous work [4] GaP nanoparticles were synthesized by similar procedures to those utilized in [5] by direct reaction of anhydrous gallium (III) chloride ($GaCl_3$) and sodium phosphide (Na_3P) in ambience of nitrogen or argon.
GaP nanoparticles are produced as a result of interaction between the (dimethylbenzene) $GaCl_3$ dissolved in the toluene and the Na_3P suspension in the solvent.

In this work we present a simple solution-phase method for the synthesis of small sizes of colloidal GaP nanoparticles by using a new precursor as a source of Ga atoms, namely the gallium acetylacetonate ($Ga[CH_3COOH=C(O\_)CH_3]_3$. The GaP nanoparticles produced by this method demonstrate a pronounced quantum confinement effect.

II. Results and discussion

Synthesis of GaP nanoparticles

GaP nanoparticles were produced by using gallium acetylacetonate ($Ga[CH_3COOH=C(O\_)CH_3]_3$ as source of Ga atoms. Initially, Na_3P is produced in a glove box as a result of a direct reaction of the sodium with the white phosphorus in the toluene solution in an inert medium as described by the following reaction:

$$12Na + P_4 = 4Na_3P \quad (1)$$

For this, an oil bath is used with magnetic stirring and heating. A round-bottom flask with three necks (Erlenmeyer flask) is placed in this bath. A thermometer and a cooler were installed on two of these necks, while the third one was used for scavenging with inert gas (argon). 0.138 g of metallic sodium (6 mmol) and 0.062 g of white phosphorus (2 mmol) are added to 20 ml of toluene.

The obtained mixture is maintained at 105°C for 2 hours under intense agitation. Afterwards, the solution is stirred, heated, and maintained at 105°C during 12 hours. As a result a black substance of Na_3P is obtained. Separately, 0.37 g of gallium acetylacetonate (1 mmol) are dissolved in 15 mL of toluene. The solution of galium acetilacetonate in toluene is stirred and heated to 110°C. Afterwards, the solution of sodium phosphide in toluene is added to the solution of galium acetilacetonate and the mixture is heated at this temperature with intensive stirring for 3 h. 0.38 g (1 mmol) of trioctylphosphine oxide (TOPO) is added to the solution as a stabilizator 5 – 10 minutes after the beginning of the syntheses process in order to avoid the agglomeration of particles. Under these conditions, the formation of GaP nanoparticles occurs according to the following reaction:

$$Ga[CH_3COOH=C(O-)CH_3]_3 + Na_3P = GaP + 3\,Na[CH_3COOH=C(O-)CH_3] \quad (2)$$

Secondary products of the reaction were sedimented in the reactor 12 hours later, and the solution becomes yellow-orange. GaP nanoparticles are segregated from this solution by means of addition of dimethylformamide and spinning at 5000 rpm.

The influence of the Ga:P ratio in the synthesis process was investigate. It was found that the optimum Ga:P ratio is 2:1.

Characterization of GaP nanoparticles

GaP nanoparticles were investigated by means of Raman scattering, EDAX, and luminescence spectroscopy under the excitation with the 325 nm line of a He-Cd laser. A luminescence band with the maximum at 420 – 420 nm was observed in the spectrum. The position of this band is shifted depending on the size of GaP nanoparticles. Data on EDAX analysis of a powder of GaP nanoparticles obtained by this method with the ration Ga:P = 2:1 are presented in Fig. 1. One can see that the oxygen line is present in the spectrum. This line is probably due to traces of oxygen in the Ar flux, which results in the production of gallium oxide or gallium phosphate in amorphous state.

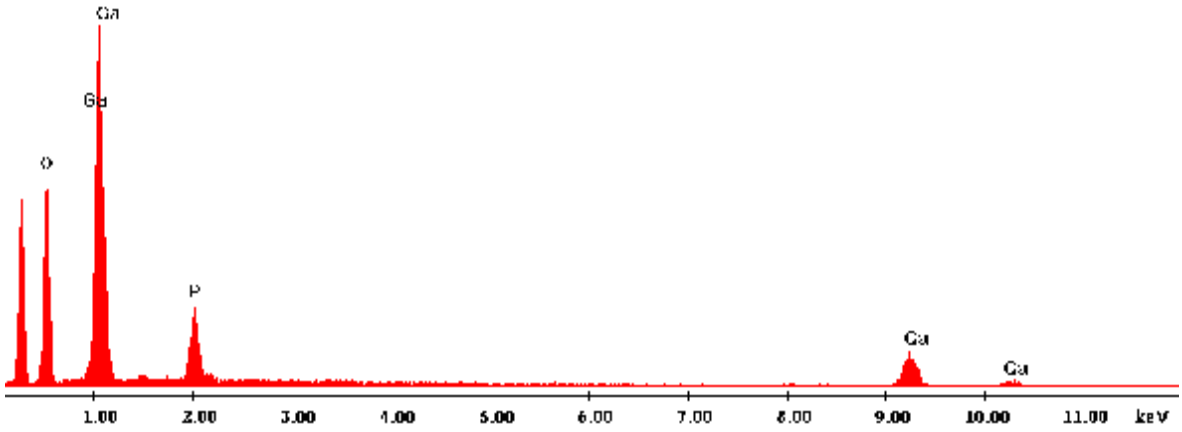

Fig. 1. EDAX spectrum for GaP nanoparticles

The X- ray diffraction spectrum of the as-obtained GaP nanoparticles is shown in Fig. 2. The XRD pattern is consistent with the cubic zinc-blend structure of GaP nanoparticles. The peak at 28° corresponds to the (111) lattice facet. The other peaks at 32, 46 and 57 are indexed as the (200), (220) and (311) reflexions, respectively.

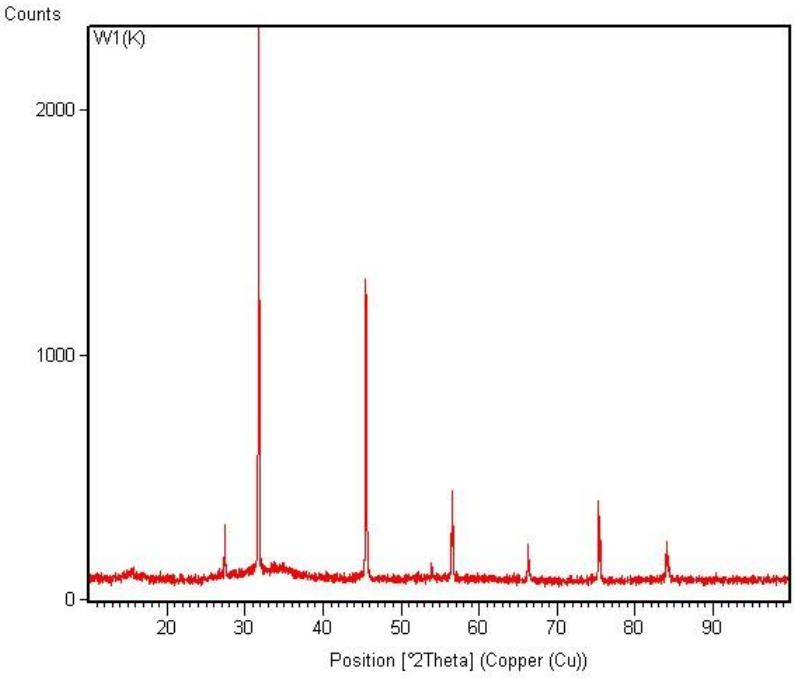

Fig. 2. XRD pattern for GaP nanoparticles.

Figure 3 presents the photoluminescence spectra of GaP nanoparticles obtained by the above described method for different Na_3P concentrations. An intensive maximum is observed at 412 nm with a shoulder at 380 nm, which correspond to nanoparticles size of ~ 3-4 nm [6]. The shit of the luminescence maximum from 445 nm in the bulk material to 380 nm in GaP nanoparticles is indicative of a pronounced quantum confinement effect).

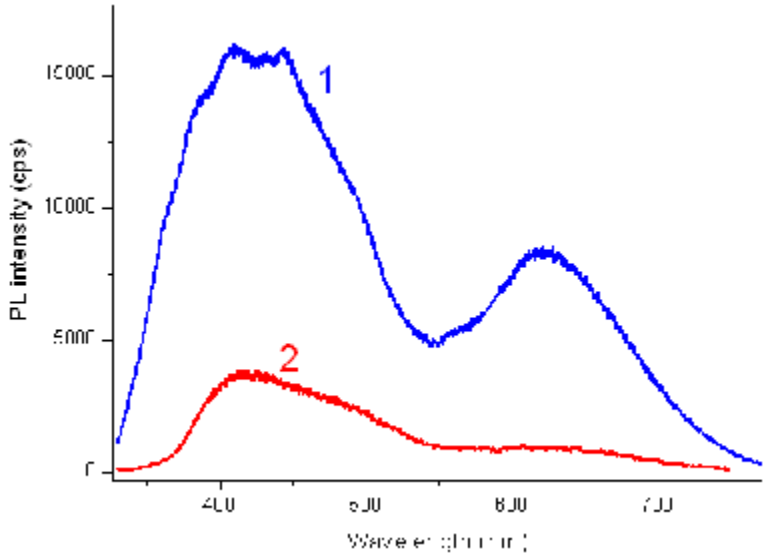

Fig. 3. Photoluminescence spectra for GaP nanoparticles under excitation of He-Cd laser. T=300K. 1 – 0.002 mol Na_3P; 2 – 0.003 mol Na_3P.

The bulk GaP is an indirect semiconductor with an indirect band gap of 2.22 eV (559 nm) and a direct band gap of 2.78 eV (446 nm) at room temperature. The shoulder at 380 nm can be attribued to the direct transitions, while the maximum of emission at the 480 nm is due to indirect transitions in the GaP nanoparticles. It is evident that a shift of both the direct (0.48 eV) and indirect (O.38 eV) band gap occurs in nanoparticles as compared to the bulk GaP.

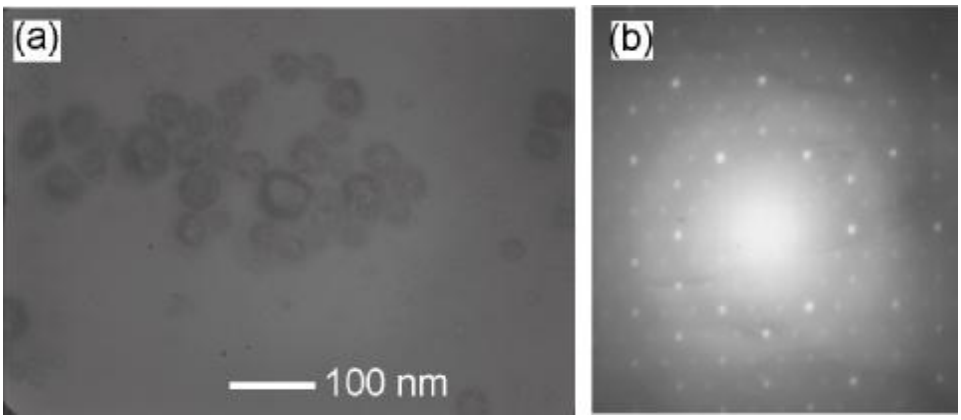

Fig. 4. A representative TEM image of GaP nanoparticles (a) with corresponding SAED pattern.

The TEM data (Fig. 4) confirm that the proposed technological method allows one to significantly reduce the size of GaP nanoparticles to 8 – 40 nm. The SAED image is indicative of crystalline nanoparticles, showing spot patterns. It is obvious that there appear three sets of diffraction patterns, and the diffraction rings can be indexed to (111), (220), and (311) planes of zinc-blende GaP.

III. Conclusions

The GaP nanoparticles prepared by colloidal low temperature method using gallium acetylacetonat as a precursor of gallium atoms and temperature treatment can be used to improve the quality of nano-suspension. A uniform fraction of nanoparticles of about 8-10 nm in diameter is produced by using gallium acetylacetonate ($Ga[CH_3COOH=C(O-)CH_3]_3$) as source of gallium atoms. These nanoparticles show an intense luminescence band with the maximum at 3.2 eV determined by quantum-confinement.

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IV. References

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