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RESEARCH OF NANOPARTICLES IN COLLOIDS SUSPENSION VIA ACOUSTIC METHOD

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Abstract

This paper states as first report in the row of detail investigations of nanoparticles behavior in solution by various resonance methods, including acoustic resonance method. Colloid suspensions of nanoparticles have been synthesized by wet chemical methods. Acoustical resonance method is used for measurement of viscoelastic properties (shear moduli and shear viscosity) of liquids.

INTRODUCTION

The investigation of low-frequency shear elasticity of liquids carried out using acoustical resonance method [1-4] give evidence that there is a low-frequency viscoelastic relaxation process in liquids with relaxation period more than one accordant to classical theories [5]. Apparently, in a number of cases, collective effects dependent on mutual position and interaction of large groups of molecules (clusters) are of resolve importance. The relaxation of non-equilibrium state of large collective requires a coordination replacement and changes of orientation of many molecules. The relaxation period may exceed the time of settled existence of separate molecules of many orders.

In the past few decades, nanostructured materials have become an attractive subject for many studies in the materials science [6]. It originates by their intermediate standing between single atom, molecule and bulk solid. Among various approaches related to the synthesis of nanomaterials, wet chemistry methods, which use the facilities of colloids chemistry and emulsions, have a number of advantages. They include an opportunity to synthesize well-separated, individual monosized nanoparticles with size less than 100 nm, stabilized by different type of surfactants, organic ligands and polymers and the comparative easiness of the morphology controlling of the growing nanoparticles.

EXPERIMENTAL RESULTS

The synthetic procedures of colloid suspensions of CdSe and $PbSO_4$ nanoparticles through wet chemistry methods are adapted. A JEOL2000EX TEM at an operating voltage 200 kV was used to characterize the morphology and size of particles. Sample for TEM measurement was prepared by dropping of the particles suspension on the copper-carbon grid with following drying at air. The qualitative identities of samples were confirmed by EDAX analysis. The crystalline structure was determined by X-ray diffraction using Cu-Kα radiation and confirmed by Raman spectroscopy measured with a triple monochromator. It was shown that spherical $PbSO_4$ nanoparticles are of 20 nm formed by primary 4 nm nanocrystals. The slight variation of synthetic conditions, namely addition of $NaNO_3$ and decrease of reaction temperature up to 0^oC leads to significant morphological changes, namely the formation of rod-like nanoparticle, where primary nanoparticles lined up on periphery.

EDAX analysis shows the presence of lead, sulfur and sodium. XRD pattern of sample shows that these particles are $PbSO_4$. It is confirmed with results of Raman spectroscopy measurements. In fig.1, Raman spectra of Lead sulfate bulk powder (a) and prepared nanopowder (b) are presented. The position of lines of Raman scattering of sample is corresponded to the vibration modes of lead sulfate of bulk powder. The small broadening and the significant shift of Raman lines to the low frequency range correlates with the small size of particles.

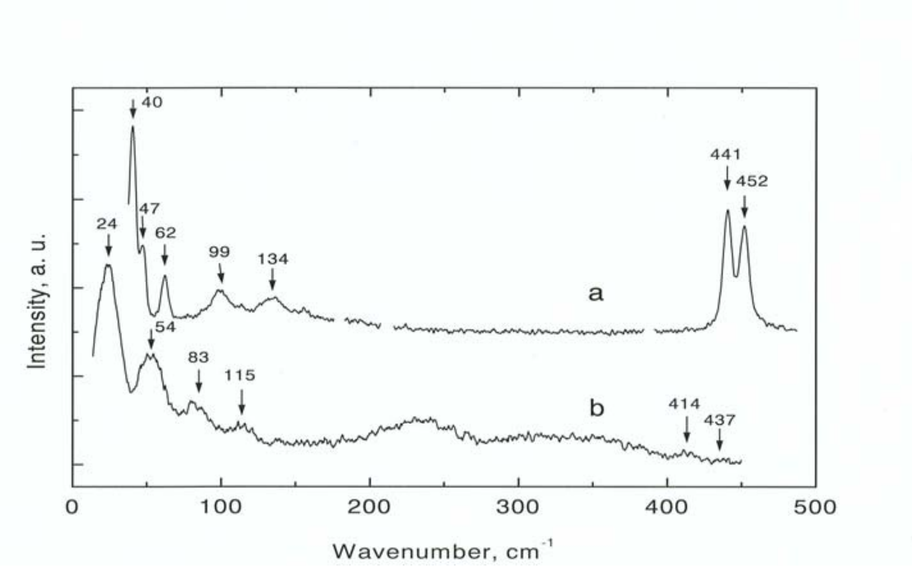
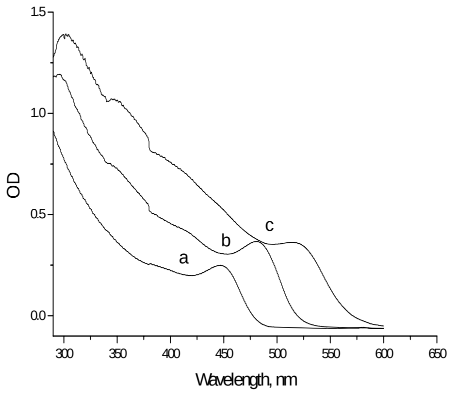


Fig.1. Raman spectra of $PbSO_4$ bulk powder (a) and nanopowder (b).

CdSe quantum dots were prepared by mixing cadmium nitriloacetate solution (Cd-NTA) with a sodium selenosulfate solution under the presence of decylamine in aqueous phase with the following rapid injection of toluene. Details of the synthesis are reported elsewhere [7]. It is known that to produce ensembles of monosized particles, technologically important step is an effective separation of nucleation and growth stages. In proposed method, this condition carries out by slow release of Cd^{2+} ions from Cd-NTA complex and careful choice of the transfer agent. Except valuable diffusion properties, this agent should possess a possibility to create a strong chemical interaction with the surface atoms of growing particles. Decylamine has been chosen as surfactant of amine group, which have required properties. The CdSe quantum dots suspensions with different sizes of 1 nm to 2.3 nm are synthesized. The corresponding optical absorption and photoluminescence spectra are shown in Fig.2. The strong quantum confinement of carriers is in consistent with blue shift of HOMO-LUMO electron energy transition reflected in optical spectra.



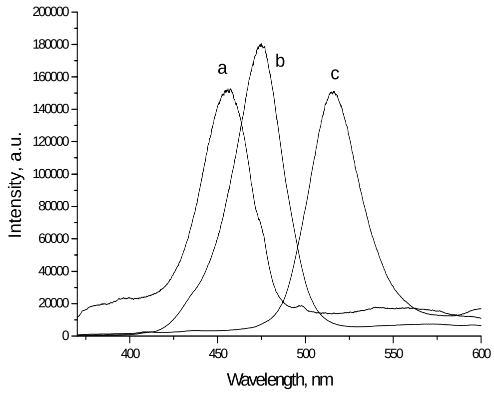


Fig.2. Optical absorption spectra (1) of CdSe dots (a -1.5 nm, b – 2 nm, c – 2.3 nm) and corresponding photoluminescence spectra (2)

Optical absorption spectra were recorded at room temperature with a Hitachi-2000 spectrophotometer [7]. Photoluminescence spectra have been measured at 4.2 and 77 K by double-grating Nalumi monochomator. 325 nm line of He-Cd laser was used as excitation source. Produced suspensions of CdSe quantum dots demonstrate textbook effect of quantum confinement and well observed as blue shift of HOMO-LUMO transition in optical spectra (absorption, emission).

The application of acoustical method for diagnostic of nanoparticle suspensions is of special interest as the addition method of value of nanoparticle size and investigation of liquid – solid transition. The system of high monodispersed and small clusters with finite number of atoms and moleculesis an ideal system in the first approximation for such investigations. The investigated object is placed between piezoquartz crystal oscillated on the basic resonance frequency and the solid cover-plate. Liquid layer is undergone to shear deformation. The components of complex shear modulus of liquid are determined by changing of acoustical properties of piezoquartz. The significant quality of this method of mechanical shear properties of liquid is that no any limitation on viscosity of investigated liquids. This method allows using liquids of 10^6 poise to 10^{-2} poise viscosity. Given acoustical resonance method is suitable for investigate the liquid layer of units to hundred microns.

The investigation of viscoelastic properties of colloid solution allows studying the dependence of viscoelastic parameters of isolate cluster – cluster crystal transition with cluster concentration change in solution. Also it allows determining the size dependence of viscoelastic properties of colloid solutions. It is expected that the features in relaxation frequency spectra at cluster – cluster crystal transition would be revealed. The certain attention would be give to investigationof shear properties in dependence on temperature and frequency of oscillation. The experimental study of these properties give an opportunity to predict the behavior of solution from proceed of chemical structure and serve as the certain criterion for produce the material with give set properties.

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REFERENCES

[1]. Badmaev B.B., Bazaron U.B., Budaev O.R. etc. “Investigation of low-frequency complex shear modulus of liquids”, Colloid. Journal, **54**, 841-846 (1982).
[2]. Badmaev B.B., Budaev O.R., Dembelova T.S. “Propagation of shear waves in polymer liquids” Acoust. Phys., **45**, 541-544 (1999).
[3]. Badmaev B.B., Damdinov B.B. “Investigation of shear-elasticity properties of organic liquids by acoustical method”, Acoust. Phys., **47**, 561-563 (2001).
[4]. Frenkel’ Ya.I. *Kinetic theory of liquids*, (Nauka, Leningrad, 1975).
[5]. Badmaev B.B., Damdinov B.B., Sanditov D.S. “Low frequency shear parameters of viscoelasticity materials”, Acoust. Phys., **50**, 156-160 (2004).
[6]. J. H. Fendler, *Nanoparticles and Nanostructured Films*. (WILEY-VCN Verlag GmbH. Weinheim,1998).
[7]. A. Kasuya, R. Sivamohan, Yu.A. Barnakov, I. Dmitruk, T. Nirasawa, V. Romanyuk, V. Kumar, S. Mamykin, K. Tohji, B. Jeadevan, K. Shinoda, T. Kudo, O. Terasaki, Z. Liu, R. Belosludov, V. Sundararajan, Y. Kawazoe, Nature Materials, **3**, 99-110 (2004).