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Far-infrared spectra of mesoporous ZnS nanoparticles

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ABSTRACT

ZnS nanoparticles were synthesized mechanochemically by high-energy milling, with three different milling times (5 min, 10 min and 20 min). Nitrogen adsorption method was used for examining specific surface area and texture of obtained powders. It was found that all samples are completely mesoporous. The optical properties were studied by far-infrared spectroscopy at room temperature in spectral region of 50–600 cm^{-1}. The analysis of the far-infrared reflectivity spectra was made by the fitting procedure. The dielectric function of ZnS nanoparticles is modeled as a mixture of homogenous spherical inclusions in air by the Maxwell-Garnet formula. In the analysis of the far-infrared reflection spectra, appearance of combined plasmon-LO phonon modes (CPPMs) with high phonon damping are observed, which causes decrease of coupled plasmon-phonon frequencies.

1. Introduction

Research on semiconductor nanoparticles has significant scientific and practical interest because of their unique optical and electrical properties [1–4]. Zinc sulfide (ZnS) is an important II–VI semiconductor which semiconductor nanoparticles has been investigated extensively because of its broad spectrum of potential applications such as in catalysts, cathode-ray tubes (CRT), field emission display (FED) phosphors for a long time. It can also be used for electroluminescent devices and photodiodes [5–12].

The differences between the nanoparticles and bulk particles are caused by a high surface to volume ratio, which induces the structural and electronic changes. These differences depend on particle sizes, shape and surface characteristics. The decrease of particle sizes causes an extremely high surface area to volume ratio. The enhanced surface area increases surface states, which change the activity of electrons and holes, and affects the chemical reaction dynamics. Consequently, much research on ZnS nanoparticles and their physicochemical properties has been carried out and various methods have been used for the preparation of these nanoparticles [13–16].

The plasmons of free carriers and the longitudinal-optical (LO) phonons interact via their macroscopic electric fields, and as the result the coupled LO phonon-plasmon modes (CPPMs) appears. The coupling of elementary excitations in solids has been investigated by many authors, and the phenomenological approach to this problem is formulated by several authors [17,18]. The most of published studies are devoted to the interaction of a single phonon with effective plasmons as well as the influence of the plasmon damping on the CPPM [19,20]. Our intention is to use far-infrared spectroscopy to study the fundamental properties of the coupled plasmon-phonons modes in the ZnS nanoparticles as well as to investigate these coupled modes under different phonon damping conditions.

In this paper, we present the results obtained by using far-infrared spectroscopy (FIR) to study optical properties of the ZnS nanoparticles which are mechanochemical synthesized using high-energy milling. Specific surface area and texture of obtained nanoparticles were examined using nitrogen adsorption method. The dielectric function of ZnS nanoparticles is modeled as a mixture of homogenous spherical inclusions in air, by the Maxwell-Garnet formula.

2. Samples preparation and characterization

Mechanochemical synthesis of ZnS nanoparticles was performed in a Pulverisette 6 planetary mill. The milling condition were: 50 balls of 10 mm diameter; weight charge of total powder mixture in the mill was 14.2 g, ball charge in the mill was 360 g, material of milling chamber and balls was tungsten carbide and

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rotation speed of the planet carrier was 500 rpm. Milling time was 5, 10 and 20 min using an argon atmosphere as a protective medium in the mill. Initial characterization of ZnS powders is presented in detail in Ref. [21]. We will briefly review results of these investigations.

The morphology of samples has been investigated by SEM using high resolution electron microscope MIRA3 FEG-SEM, Tescan at accelerating voltage lower than 29 kV. From micrographs (Fig. 1) we conclude that ZnS powder is composed by well-defined and separated nanoparticles. These nanoparticles are spherical and have about 2 nm of diameter.

High resolution TEM (HRTEM-Philips Tecnai 200 operated at 200 kV) images provide the determination of the size of the nanoparticles, the type of structures produced and also the possibly induced morphologies (Fig. 2) [22]. Several clusters are clearly identified, and particularly three of them are having sizes of 2.6, 3.7 and 3.4 nm respectively. The corresponding fast Fourier transform (FFT) denotes a polycrystalline material, which must be composed of the nanocrystals.

The structural characteristics were obtained by the XRD powder technique. All samples were examined under the same conditions, using a Philips PW 1050 diffractometer equipped with a PW 1730 generator, 40 kV × 20 mA, using Ni filtered CoKα radiation of 0.1778897 nm at room temperature. Diffraction patterns show mainly the reflection of cubic phase (Fig. 3). The refracting planes denoted with (hkl) indices are 111, 220 and 311, respectively. Crystallite sizes were estimated as 1.9 nm (after 5 min milling time), 2.3 nm (10 min) and 2.4 nm (20 min).

3. Results and discussion

3.1. Adsorption isotherms - BET experiments

The specific surface area and the pore size distribution (PSD) of ZnS were analyzed using the Surfer (Thermo Fisher Scientific, USA). PSD was estimated by applying BJH method [23] to the desorption branch of isotherms and mesopore surface and micropore volume were estimated using the t-plot method [24]. Nitrogen adsorption isotherms for ZnS nanoparticles, as the amount of N_2 adsorbed as function of relative pressure at −196 °C, are shown in Fig. 4. According to the IUPAC classification [25] isotherms of ZnS samples are of type IV and with a hysteresis loop which is associated with mesoporous materials. In all samples, the shape of hysteresis loop is of type H3. Isotherms revealing type H3 hysteresis do not exhibit any limiting adsorption at high P/P_0, which is observed with non-rigid aggregates of particles giving rise to slit-shaped pores [26]. Specific surface areas calculated by BET equation, S_{BET}, are listed in Table 1. S_{BET} values, for all samples, lie within 41–72m^2 g^{-1}. Overall specific surface decrease with the increase of milling time. r_{med} is the median pore radius and this value is the largest in the case of the sample obtained after 10 min of the mechanochemical treatment. PS confirms this conclusion i.e., pore radii are in the wide region from 2 to 45 nm.

Pore size distribution (PSD) of samples is shown in Fig. 5. Figure shows that samples are mesoporous with most pore radius between 2 and 46 nm. Mean pore radius for all samples, as well as cumulative pore volume (CpV) are presented in Table 1. As expected, CpV decrease with increasing the milling time.

t-plots, obtained on the basis of the standard nitrogen adsorption isotherms, are shown in Fig. 6. The straight line in the medium t-plot region gives a mesoporous surface area including the contribution of external surface, S_{meso}, determined by its slope, and the micropore volume, V_{mic}, is given by the intercept. The calculated porosity parameters (S_{meso}, S_{mic}) are given in Table 1 t-plot analysis confirmed that all samples are completely mesoporous (pore radius is between 2 and 50 nm).

3.2. Far-infrared spectroscopy

The far-infrared measurements were carried out with a BOMEM DA − 8 FIR spectrometer. A DTGS pyroelectric detector was used to cover the wave number range from 50 to 600 cm^{-1}.

When visible light interacts with semiconducting nanoparticles (characteristic size d, dielectric function ε_2) which are distributed in a medium with the dielectric constant ε_1 in the limit $\lambda >> d$, the heterogeneous composite can be treated as a homogeneous medium and effective medium theory is applied. There are many mixing models for the effective dielectric permittivity of such a mixture [27]. Since our samples are well defined and separated nanosized grains we used Maxwell-Garnet model for present case. For the spherical inclusions case, the prediction of the effective permittivity of mixture ε_{eff} according to the Maxwell-Garnet mixing rule is [28]:

$$\varepsilon_{eff} = \varepsilon_1 + 3f\varepsilon_1 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1 - f(\varepsilon_1 - \varepsilon_2)} \quad (1)$$

Here, spheres of permittivity ε_2 are located randomly in homogeneous environment ε_1 and occupy a volume fraction *f*.

The ZnS nanoparticles are situated in air, therefore the ε_1 is 1. Dielectrical function of ZnS nanoparticles (ε_2) we obtain by applying following procedure. The low-frequency dielectric

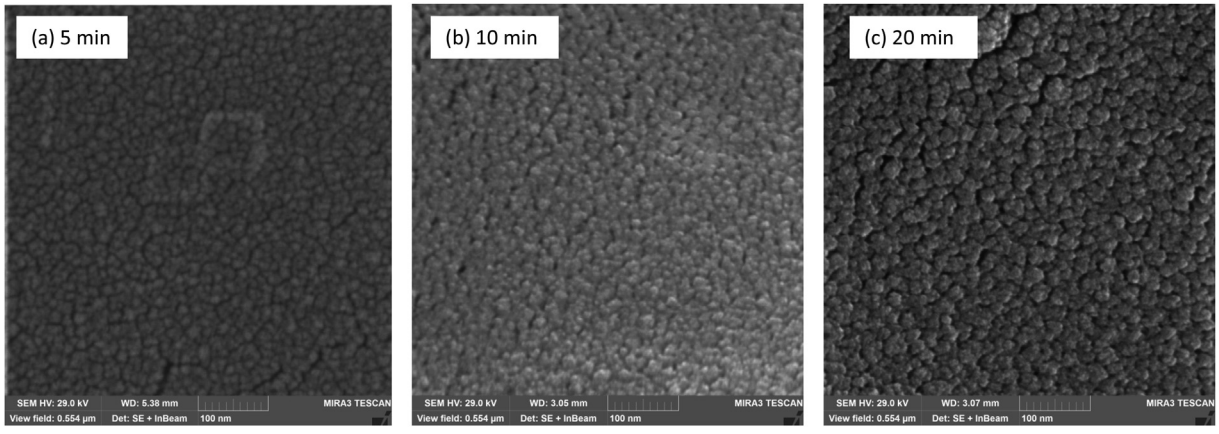

Fig. 1. SEM images of ZnS nanoparticles obtained after milling time of 5 min (a), 10 min (b) and 20 min (c) [21].