Comparative study of Raman properties of various lead sulfide morphologies

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ABSTRACT:
Lead sulfide (PbS) nanostructures are one of the possible candidates to be used in modern optic devices. It can be deposited by various methods. Composition of the deposited layers and their optical properties can be determined by Raman spectroscopy. In this work, Raman features of PbS nanostructures are discussed in detail. Several different morphology of PbS nanostructures such as nonocubics, hexapod and octahedron was studied. Their size and morphologies are expressed and discussed about their Raman spectrum. In each case, represented the reason of the any Raman peaks and finally, it has been tried to be a comparison between them.

KEYWORDS: Nanostructures; Quantum confinement; Lead sulfide; Raman spectroscopy; Optical applications; Morphology; Optical phonon; Surface phonon; X-ray diffraction; Raman peaks.

1. INTRODUCTION

During the past years, much investigation has been done on nanostructures. These investigations are outcome of the transition from micro-particles phase to nano-particles phase and exhibit various properties from nanostructure. For this reason the nanostructures have attracted the attention of many researchers. In nano-phase with by increasing the surface to volume ratio, quantum confinement appears. Therefore recognition and controlling of them is very important.

Among these compound semiconductor nanostructures are important. Lead Sulfide (PbS) is one of these compound semiconductors with narrow band gap (0.41ev) [1] that have important optical applications such as solar cells and infrared detectors [2], solar control coatings [3] optical fibers and broadband optical amplifiers [4]. So far various forms of PbS nanostructures with various method such as chemical bath deposition (CBD) [5], electrochemical deposition [6] hydrothermal [7] and vacuum evaporated [8] have been reported.

It has been demonstrated that Raman spectroscopy is a fast, nonintrusive and nondestructive tool for appreciating optical properties of nanostructures. In fact Raman spectroscopy gives us information about the phase composition of the deposited material. Raman spectroscopy is used to identify the molecular structure, rotational frequencies, geometric evaluation and even molecular symmetry. In a crystalline semiconductor the observed Raman shifts usually correspond to the longitudinal optical phonons (LO), whereas, other modes, such as the transverse optical phonons (TO) and the surface phonons (SP), in general, not observable because of symmetry restrictions and low intensities, respectively. However, as the surface-to-volume ratio is large for nanostructures materials, it is possible to observe the SP mode by Raman scattering measurements. In Raman spectra the surface roughness as well as the crystal size also plays important role [9]. According to the group theory, single crystalline PbS belongs to the Fm3m space group, with cubic rock salt structure.

In this paper optical properties of three different morphology of PbS nanostructure were investigated by Raman spectra analysis. Frequency bands have been studied and tried to be a comparison between them. For all sample Raman spectra were measured at the room temperature by a Jobin-Yvon Lab RAM HR Raman spectrometer with 632.8 nm excitation wavelength.

2. PBS NANOCUBICES

These nanostructures grown by Chen *et al* [10]. PbS nanocrystals (NCs) were formed by using Pb nanowires reacted with hydrogen sulfide (H_2S) gas (chemical deposition).Fig.1 present scanning electron microscopy (SEM) images of these PbS NCs. The morphology of the PbS NCs in Fig.1 is cubic-shaped particles with 50-100 nm diameters. X-ray diffraction (XRD) analysis confirmed the formation of PbS nanoparticles (JCPDS No. 03-0665) with the lattice constant a = 0.59362 nm.

Fig. 2 shows the Raman spectra of deposited PbS NCs. Two bands at 212 and 451 cm^{-1} are attributed to the scatterings of the longitude optic (1LO) phonon and 2LO phonon of PbS, respectively. A weak band at 151 cm^{-1} assigns to be a combination of transverse acoustic (TA) and transverse optic (TO) phonons [8]. The TO and SP modes are difficult to observe in the Raman spectrum due to the symmetry restrictions and low intensities, respectively. If the surface to volume ration is large, it will be possible to observe SP mode in the Raman spectrum. In this work, there is a peak at 194 cm^{-1} owing to the SP phonons [10].

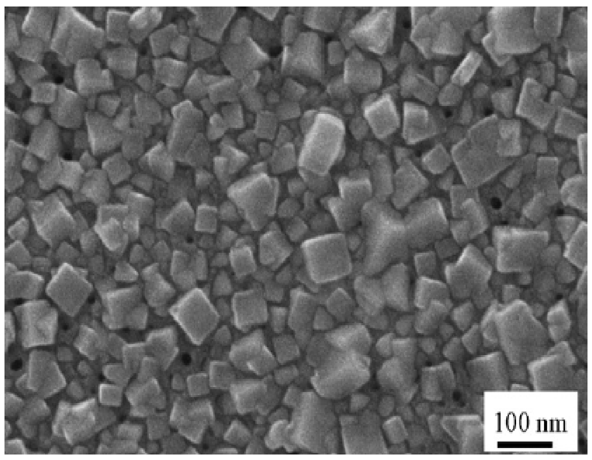

Fig. 1. SEM image of PbS NCs.

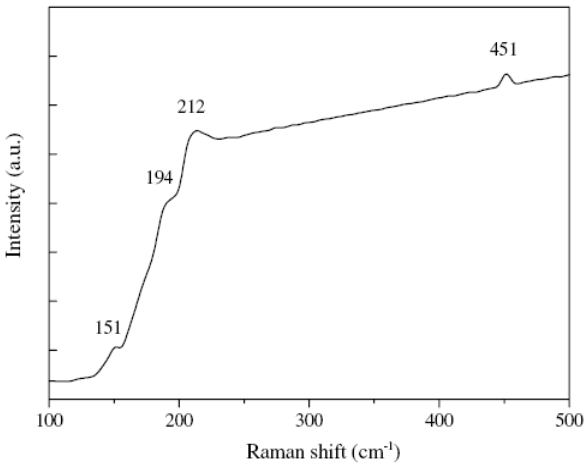

Fig. 2. Raman spectra of PbS cubic-shaped NCs.

3. PBS HEXAPOD NANOSTRUCTURES

These nanostructures grown by Zhang *et al* [11]. Their growth method has been chemical deposition (CD).

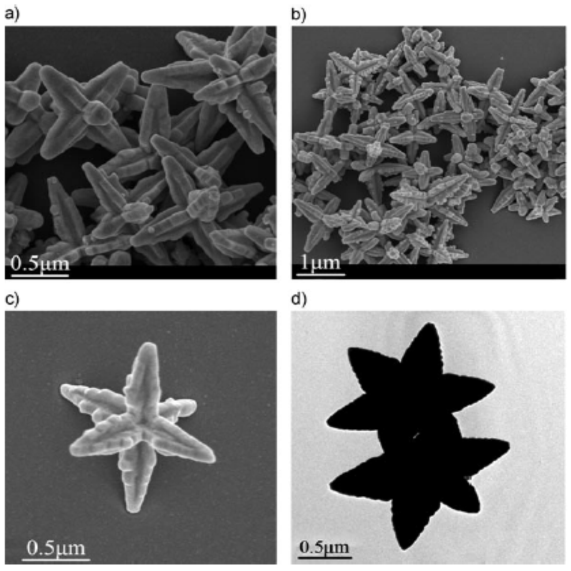

Fig. 3. SEM and TEM images of the PbS hexapod structures.

Fig. 3 (a, b, c and d) presents SEM and transfer electron microscopy (TEM) images of this PbS nanostructures. The morphology of them is high regular hexapod-like structures. According to these images, the length of arms and diameter of the hexapod-shape structures is about 300-600 nm and 1.4 μm, respectively. XRD analysis confirmed the formation of face-center-cubic structure of PbS with lattice constant a=0.5923, which is in good agreement with the literature value (JCPDS No. 78-1899).

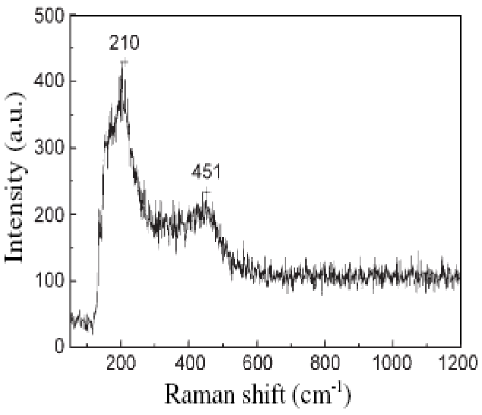

Fig. 4. Raman spectra of PbS hexapod structures.

Fig. 4 shows the Room temperature Raman spectra of PbS hexapod structures. The strong peaks at 210 and 451 cm^{-1} were clearly observed from Figure 4 which is attributed to 1LO phonon mode and 2LO phonon mode, respectively [11]. In comparison with previous work, for the PbS nanostructures, Raman peaks at 210, 271, 451 cm^{-1} should be observed due to a 1LO phonon mode, a 2 phonon process, and a 2LO phonon mode, respectively. But in this result the peak at 210 cm^{-1} was so intense that the peak at 271 cm^{-1} was difficult to characterize.

4. PBS OCTAHEDRON NANOCRYSTALS

These nanocrystals grown by Wang *et al* [12]. Their growth method has been CD by a Simple Solution Route. Fig. 5 (A and B) presents field emission scanning electron microscopy (FESEM) images of these PbS nanoparticles. The morphology of them is a simple and amazingly well-defined uniform truncated octahedron structure with 14 faces. Each truncated octahedron has a composition of six squares and eight hexagons, and the overall structure shares 24 identical edges (Figure 4A). Diameter of each octahedron structures and each square is about 210-220 nm and 90 nm, respectively. XRD analysis confirmed the formation of standard face-center-cubic (fcc) structure of PbS (space group: Fm3m, a=0.5936 nm, JCPDF 05-0592).

Fig. 6 shows the Raman spectra of PbS octahedron structures. The strong peaks at 190 cm^{-1} should be due to the SP mode, and its intensity increases greatly with the decreasing crystal size, and the SP mode is so intense that the peaks at 210 and 271 cm^{-1} become two small shoulders and are difficult to characterize [12].

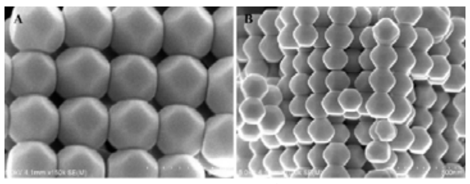

Fig. 5. FESEM images of the nanocrystals.

A weak and wide peak at 440 cm^{-1} and a strong and intense peak at 602 cm^{-1} are from 2LO and 3LO phonon modes, respectively [7]. Strong peak at 966 cm^{-1} may be attributed to the photodegradation of PbS [9].

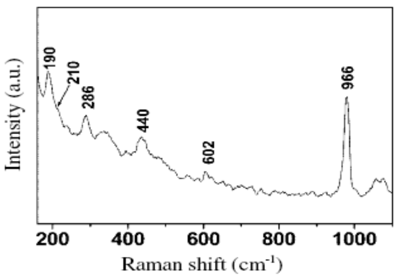

Fig. 6. Raman spectra of the PbS octahedron nanocrystals.

5. CONCLUSION

In summary, Raman studies have been performed on PbS nanostructures. The morphology of these PbS nanostructures is cubic-shaped, hexapod-like and octahedron structures. Raman spectra were measured by a Jobin-Yvon Lab RAM HR Raman spectrometer with 632.8 nm excitation wavelength. The number of the Raman peak whit size increasing in PbS hexapod nanostructures has a decreasing. This phenomenon may be due to reduced surface to volume ratio and a decrease in the quantum limit. The mode of 2LO phonon mode observed in all sample. In two samples, cubic-shaped and hexapod-like structures the 2LO phonon mode and in other two samples, cubic-shaped and octahedron structures the SP mode have observed.

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