Study of optical phonon modes of CdS nanoparticles using Raman spectroscopy

RAJEEV R PRABHU and **M ABDUL KHADAR***

Department of Physics, Centre for Nanoscience and Nanotechnology, University of Kerala,
Kariavattom PO, Thiruvananthapuram 695 581, India

Abstract. The reduction in the grain size to nanometer range can bring about radical changes in almost all of the properties of semiconductors. CdS nanoparticles have attracted considerable scientific interest because they exhibit strongly size-dependent optical and electrical properties. In the case of nanostructured materials, confinement of optical phonons can produce noticeable changes in their vibrational spectra compared to those of bulk crystals. In this paper we report the study of optical phonon modes of nanoparticles of CdS using Raman spectroscopy. Nanoparticle sample for the present study was synthesized through chemical precipitation technique. The CdS nanoparticles were then subjected to heat treatment at low temperature (150°C) for extended time intervals. The crystal structure and grain size of the samples were determined using X-ray diffraction and HRTEM. The Raman spectra of the as-prepared and heat treated samples were recorded using conventional Raman and micro-Raman techniques. The spectrum of as prepared sample exhibited an intense, broad peak at 301 cm^{-1} corresponding to the LO phonon mode. Higher order phonon modes were also observed in the spectra. A noticeable asymmetry in the Raman line shape indicated the effect of phonon confinement. Other features in the spectra are discussed in detail.

Keywords. Nanoparticles; optical phonons; cadmium sulfide; Raman.

1. Introduction

Semiconductor nanoparticles form an important class of materials because of their interesting physical properties and their technological applications (Brus 1986; Henglein 1989; Weller 1993; Alivisatos 1996). Quantum size effects exhibited by semiconducting nanoparticles have been at the centre of scientific interest for the past two decades. In these investigations, vibrational spectroscopy has played a vital role as quantum size effect which results from confinement of electrons, holes and phonons within the nanoparticles efficiently show up their signature in this type of spectroscopy. During the last few years, studies of quantum size effects are mainly focused on the observation of the shift and modification of the Raman peaks since, in addition to revealing the effects of finite size of the particles on the vibrational modes and exhibiting additional features arising from their large values for surface to volume ratio, it can probe the local vibrational environment.

Confinement of electrons, holes and vibrations to crystallites of size a few nanometers brings about dramatic changes in their optical properties (Murray *et al* 1993; Wang *et al* 2002). Confinement of charge carriers appears as a blue shift of the bandgap and can be observed in the absorption spectra. The coupling of confined electrons and confined phonons is another factor that determines the optical properties of nanoparticles.

Only the zone centre optical phonons can be observed in ideal single crystals using Raman spectroscopy. But in nanocrystalline materials, $q \approx 0$ selection rule is relaxed due to interruption of lattice periodicity. It has been theoretically calculated and experimentally observed that as the particle size reduces, the Raman spectra develop marked asymmetry towards the low frequency side and exhibit a frequency shift also towards the low frequency side. In addition to the optical phonons, the acoustic phonons also are confined within the crystallites of nanostructured materials, when the grain sizes are very small (Nemanich *et al* 1981; Richter *et al* 1981; Duval *et al* 1986; Roy and Sood 1996). The confinement of acoustic phonons results in the appearance of frequencies which depend on the elastic properties of the material through longitudinal and transverse sound velocities. For particles of diameter <10 nm, the frequencies of these modes fall between 5 and 50 cm^{-1} and as a result, these modes are observable using Raman spectroscopy. The interesting feature of these frequencies is that they depend on the reciprocal of the particle size and this relation has been experimentally verified in several cases (Roy and Sood 1996).

Although the vibrational properties of nanoparticles have been extensively studied using conventional Raman spectroscopy, such samples have not been examined simultaneously using micro-Raman technique for probing the effect of high intensity of illumination in exciting Raman

---

*Author for correspondence (mabdulkhadar@rediffmail.com)

features of higher orders. In addition, even though the effect of high temperature heat treatment of nanoparticles of CdS on their Raman spectra have been extensively studied (Sivasubramanian *et al* 2006), such studies on CdS nanoparticles subjected to low temperature heat treatment for long periods have not been reported in the literature. In the present study, CdS nanoparticles are prepared using a simple chemical route. These particles are then heat treated in an attempt to study the effect of low temperature heat treatment on the crystal structure and other properties of the nanoparticle sample. The vibrational spectra of the as-prepared and heat treated samples are then recorded using conventional Raman spectroscopy as well as micro-Raman spectroscopy and these spectra are analysed.

2. Experimental

Nanoparticles of CdS were prepared in an aqueous medium through chemical precipitation technique starting from analar grade cadmium salt and sodium sulfide, and using triethanolamine as capping agent (Prabhu and Abdul Khadar 2005). The particles were then heat treated at 150°C in DMSO for 4, 8 and 16 h. The XRD patterns of the samples were recorded using Bruker diffractometer and CuKα radiation. The as-prepared and heat treated samples were examined using JEOL-3010 HRTEM. The Raman spectra of these samples were recorded using SPEX Ramalog spectrometer using a 514 nm excitation line. Also the micro-Raman spectrum of a sample was recorded using a Renishaw Ramascope Olympus DHZ-UMA spectrometer using a 514 nm excitation line.

3. Results and discussion

The XRD patterns of the as-prepared and heat treated samples of nanoparticles of CdS are shown in figure 1. The XRD patterns of the CdS samples in figures 1a, b, c are identical and they exhibit broad peaks centred at 2θ values of 26·60, 44·30 and 52·03° and a shoulder at $\sim 31·5°$ which could be indexed to scattering from 111, 220, 311 and 200 planes, respectively of cubic CdS. The absence of peaks at 28·4 and 53°, which are associated only with hexagonal phase, eliminates the possibility of incorporation of hexagonal phase of CdS in the samples. When the duration of heat treatment is increased to 16 h partial conversion of CdS from cubic to hexagonal phase is identified (figure 1d). The grain size of the CdS nanoparticles is calculated for as-prepared and heat treated samples using the Scherrer equation (Cullity and Stock 2001) and is found to be ~ 3 nm. Low temperature annealing has not produced any grain growth. Hall-Williamson plot of as-prepared sample (figure 2) has a negative slope indicating compressive strain experienced by the particles.

Figure 3 shows HRTEM images of as prepared nanoparticles and those of the sample heat treated at 150°C for 8 and 16 h. The images clearly show lattice fringes indicating good crystallinity of the samples. The TEM images give a grain size of ~3 nm in agreement with XRD measurements.

The Raman spectra of the nanoparticle samples of CdS recorded in the 1 LO mode region are shown in figure 4. The 1 LO peak centred around 300 cm^{-1} for the as prepared sample shows a small degree of asymmetry towards low frequency region. Although the positions of the
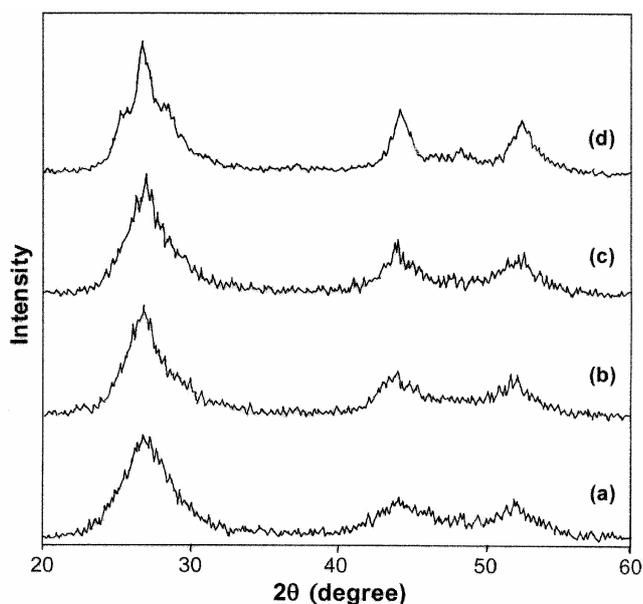

Figure 1. XRD patterns of nanoparticles of CdS: (a) as-prepared sample, (b) sample heat treated for 4 h, (c) sample heat treated for 8 h and (d) sample heat treated for 16 h.
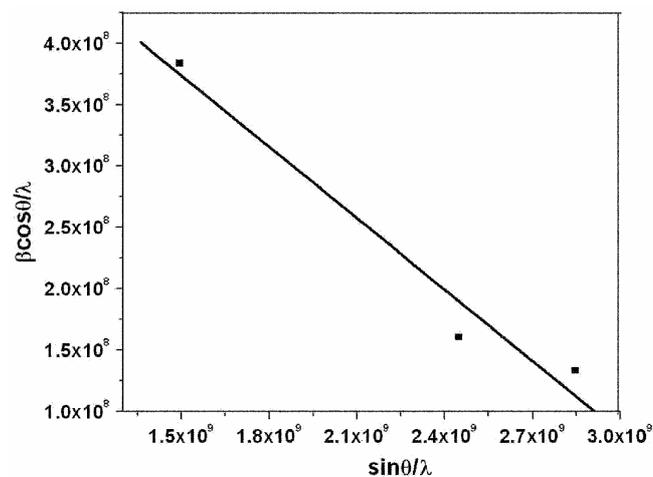

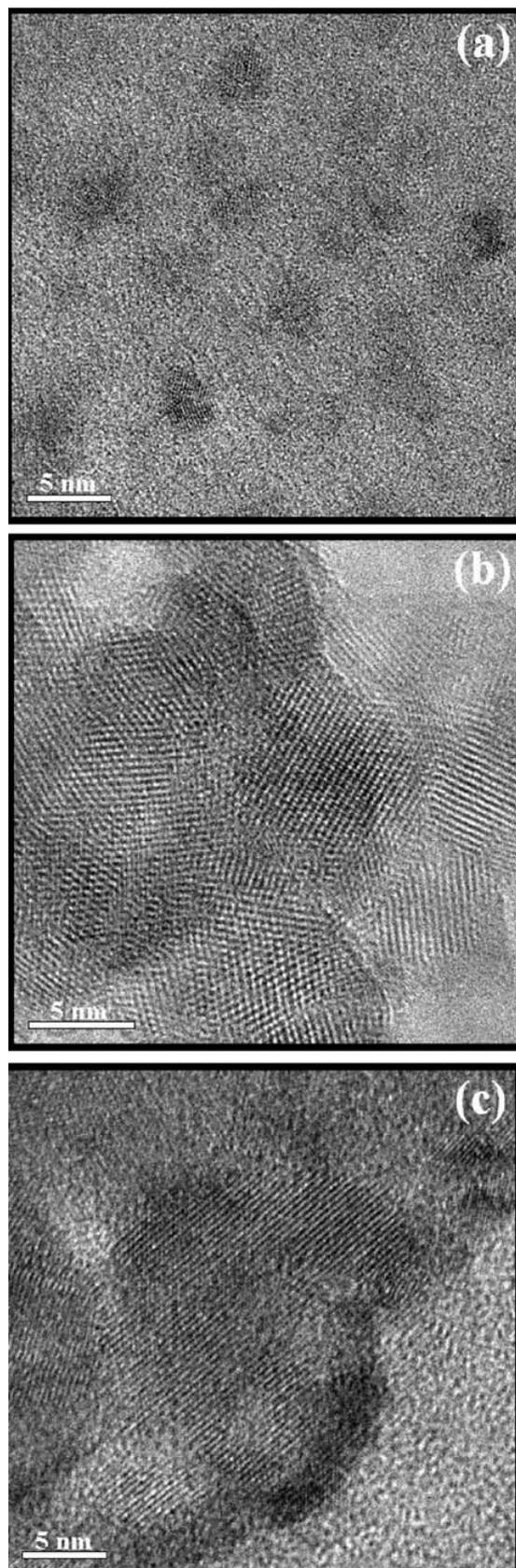**Figure 2.** Hall–Williamson plot for as-prepared nanoparticles of CdS.

peaks are unchanged, the width (FWHM) decreased by noticeable amount on heating the samples. 1 LO peak of CdS is reported to appear around 300 cm^{-1} in micron and nanometer sized particles and is the prominent peak in all the reported results on CdS samples (Chuu *et al* 1991; Chuu and Dai 1992; Abdul Khadar and Thomas 1995; Nandakumar *et al* 2001). Figure 5 shows the micro-Raman spectrum of the CdS nanoparticles heat treated for 16 h. The peaks are obtained at 301, 603 and 909 cm^{-1} corresponding to 1 LO, 2 LO and 3 LO optical phonons, respectively.

From figure 4 it is seen that the first order LO Raman line is not only broadened, but also it shows an asymmetric broadening towards the low frequency side. The 1 LO phonon frequency for a single crystal of CdS was reported as 305 cm^{-1} (Tell *et al* 1966), while the value obtained in the present study is around 300 cm^{-1}. This frequency shift of the 1 LO Raman peak in CdS nanoparticles has been studied before and is mainly ascribed to the grain size effect (Chuu and Dai 1992). It is found from figure 4 that
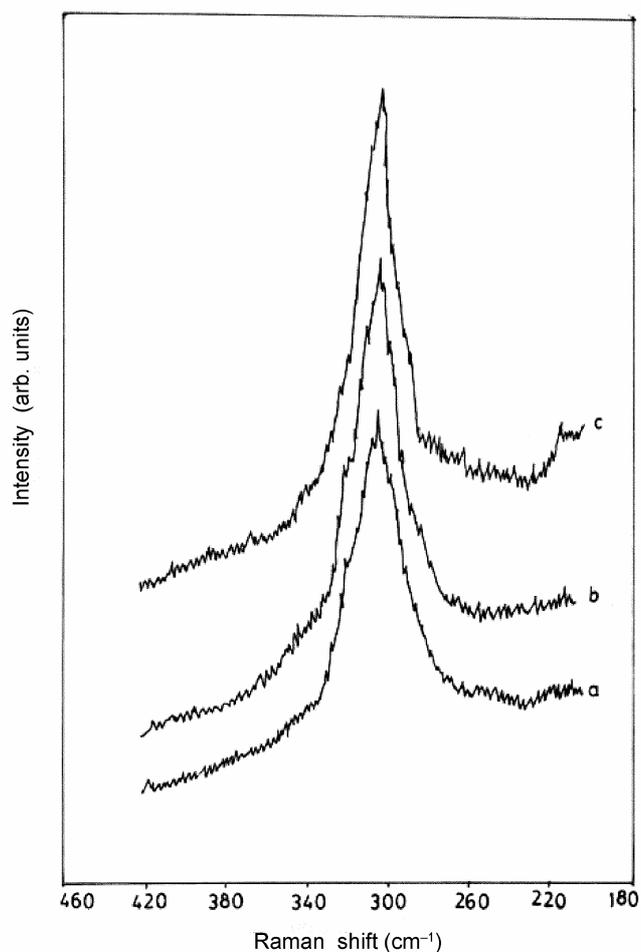

Figure 3. HRTEM images of nanoparticles of CdS: (**a**) as-prepared CdS nanoparticles, (**b**) sample heat treated for 8 h and (**c**) sample heat treated for 16 h.

Figure 4. Raman spectra of CdS nanoparticles. **a**. As-prepared sample, **b**. sample heat treated for 4 h and **c**. sample heat treated for 8 h.

the position of these 1 LO peak does not undergo any shift for the heat treated samples but their FWHM has decreased noticeably compared to that of the as-prepared sample. It is now well known that confinement of phonons, optical as well as acoustic, influences the phonon spectra conspicuously when the grain size falls to a few nanometers. Confinement of optical phonons causes an asymmetry in the line shape and a shift towards the low frequency side compared to that for bulk CdS. In bulk crystals, the phonon eigen state is a plane wave and the selection rule for Raman scattering is $q \approx 0$, where q is the wave vector. But in nanocrystallites, the spatial correlation function of the phonons is finite due to the phonon confinement, and hence $q \approx 0$ selection rule is relaxed and Raman signals from the phonon branch away from the zone centre also contribute to the resultant Raman line. The net effect of this contribution is the development of a marked asymmetry of the Raman line towards the low frequency side and a shift in the peak position which also is towards the low frequency side. Quantitative descriptions of the effect of phonon confinement on the Raman spectra of nanostructured materials including CdS (Arora *et al* 2004) have been reported by different researchers (Richter *et al* 1981; Campbell and Fauchet 1985).

In nanoparticles, the surface layers occupy a large percentage of the total volume of the material. It is known that the atomic arrangement on and near the grain boundaries is far from equilibrium and hence the Raman signals from these layers may be more similar to those from amorphous structures than those from crystalline ones (Bobovich 1988). If these surface layers of the nanoparticles have a chance to acquire a more ordered arrangement, then their contribution to the width of the Raman lines should decrease. Figure 4 shows that, the FWHM of the Raman lines noticeably decreases on increasing the duration of heating. It may be noted that, in
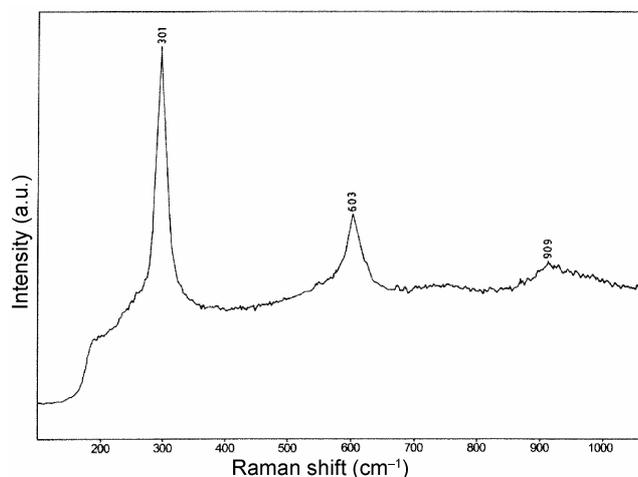
this study, the temperature of heat treatment is kept low (150°C) to prevent grain growth. As seen from the XRD patterns in figure 1, the grain sizes of the particles have not changed appreciably due to heat treatment but the heat treatment has caused an improvement of the crystallinity of the nanoparticles and also a partial phase change (figure 1d). This leads to the inference that the heat treatment of the samples have caused a more regular arrangement of the atoms in the surface layers of the nanoparticles and to a partial change in the crystal structure and reduction of defect density. The X-ray diffraction patterns (figure 1d) and HRTEM pictures (figure 3c) clearly indicate a partial change of phase on heat treatment of the sample. The decrease in the FWHM of the 1 LO Raman line with heat treatment may be due to this partial change in the crystal structure and reduction of defect density. The broadening of the spectra, the asymmetry of the line shape and the shift of the peak towards lower frequency may be attributed to optical phonon confinement (Arora *et al* 2007).

Leite *et al* (1969) reported intensity measurements of nth order Raman scattering features ($n = 1, 2 \ldots 9$) in CdS crystals as a function of temperature and laser frequency. The lines higher than second-order disappeared when the laser frequency was far below $E_g/\hbar$, where E_g is the bandgap. Abdi *et al* (2006) recently reported three orders of Raman peaks associated with LO phonons of CdS nanorods at 301, 603 and 906 cm^{-1} when excited with laser light of wavelength, 496 nm. Bischof *et al* (1997) have studied the intensity dependent micro-Raman spectra of CdS$_x$Se$_{1-x}$ nanocrystals embedded in borosilicate glass matrix and found a linear dependence of the Raman signal on laser intensity under weak laser excitation while the Raman intensity deviated from the linear behaviour for high laser intensities. In the present study, we observed that the micro-Raman spectra of nanoparticles of CdS clearly showed first, second and third order LO Raman peaks when excited using laser light of wavelength, 514 nm. XRD and HRTEM results indicate a grain size of ~ 5 nm for the particles of CdS which corresponds to a bulk bandgap of ~ 2.4 eV. The energy of the laser (wavelength 514 nm) is close to the bandgap of CdS nanoparticles and the excitation of three orders of the longitudinal optical phonon modes in the Raman scattering spectrum of nanoparticles of CdS in the present study is attributed to resonance effects or high laser power intensity in the micro-Raman experiment or both.

4. Conclusions

Nanoparticles of CdS are synthesized through chemical precipitation technique. The particles are heat treated at 150°C for different time durations. The particles are characterized by XRD and HRTEM. Dispersive Raman and micro-Raman spectra of the samples are recorded and

Figure 5. Micro-Raman spectrum of CdS nanoparticles heat treated for 16 h.

analysed. A marked asymmetry in the Raman line shape indicated the effect of phonon confinement. The micro-Raman spectra of nanoparticles of CdS clearly show first, second and third order LO Raman peaks when excited using laser light of wavelength, 514 nm. The excitation of three orders of the longitudinal optical phonon modes in the Raman scattering spectrum of nanoparticles of CdS in the present study is attributed to resonance effects.

Acknowledgements

References

Abdi A, Titova L V, Smith L M, Jackson H E, Rice J M Y, Lensch J L and Lauhon L J 2006 *Appl. Phys. Lett.* **88** 043118
Abdul Khadar M and Thomas B 1995 *Nanostruct. Mater.* **5** 289
Alivisatos A P 1996 *Science* **271** 933
Arora A K, Rajalakshmi M and Ravindran T R 2004 in *Encyclopedia of nanoscience and technology* (ed.) H S Nalwa (Los Angeles: American Scientific Publishers) **Vol. 8,** p. 499
Arora A K, Rajalakshmi M, Ravindran T R and Subramanian V 2007 *J. Raman Spectrosc.* **38** 604
Bischof T, Lermann G, Schreder B, Materny A, Kiefer W and Ivanda M 1997 *J. Opt. Soc. Am.* **B14** 3334
Bobovich Ya S 1988 *J. Appl. Spectrosc. (USA)* **49** 869
Brus L 1986 *J. Phys. Chem.* **90** 2555
Campbell H and Fauchet P M 1986 *Solid State Commun.* **58** 739
Cullity B D and Stock S R 2001 *Elements of X-ray diffraction* (New York: Prentice Hall Publishers) 3rd ed., p. 664
Chuu D R and Dai C M 1992 *Phys. Rev.* **B45** 11805
Chuu D R, Dai C M, Hsieh W F and Tsai C T 1991 *J. Appl. Phys.* **69** 8402
Duval S, Boukenter A and Champagnom B 1986 *Phys. Rev. Letts* **56** 2052
Henglein A 1989 *Chem. Rev.* **89** 1861
Leite R C C, Scott J F and Damen T C 1969 *Phys. Rev. Letts* **22** 780
Murray C B, Norris D J and Bawendi M G 1993 *J. Am. Chem. Soc.* **115** 8706
Nemanich J, Solin S A and Martin R M 1981 *Phys. Rev.* **B23** 6348
Nandakumar P, Vijayan C, Rajalakshmi M, Arora A K and Murti Y V G S 2001 *Physica* **E11** 377
Prabhu Rajeev R and Abdul Khadar M 2005 *Pramana-J. Phys.* **65** 801
Richter H, Wang Z P and Ley L 1981 *Solid State Commun.* **39** 625
Roy A and Sood A K 1996 *Phys. Rev.* **B53** 12127
Sivasubramanian V, Arora A K, Premila M, Sundar C S and Sastry V S 2006 *Physica* **E31** 93
Tell B, Damen T C and Porto S P S 1966 *Phys. Rev.* **144** 771
Wang W, Germanenko I and Shall M S E 2002 *Chem. Mater.* **14** 3028
Weller H 1993 *Adv. Mater.* **5** 88