A Raman Study of CdSe and ZnSe Nanostructures

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Raman studies have been carried out on CdSe nanotubes and ZnSe nanorods produced by surfactant-assisted synthesis. The Raman spectrum of CdSe nanotubes shows modes at 207.5 and 198 cm^{-1}; the former arises from the longitudinal optic phonon mode red-shifted with respect to the bulk mode because of phonon confinement, and the latter is the $l = 1$ surface phonon. Analysis based on the phonon confinement model demonstrates that the size of the nanoparticle responsible for the red-shift is about 4 nm, close to the estimate from the blue-shift of the photoluminescence. The Raman spectrum of ZnSe nanorods shows modes at 257 and 213 cm^{-1}, assigned to longitudinal and transverse optic phonons, blue-shifted with respect to the bulk ZnSe modes because of compressive strain. The mode at 237 cm^{-1} is the surface phonon.

Keywords: Raman Spectroscopy, Nanorods, CdSe, ZnSe, Phonon Confinement, Semiconducting Nanoparticles.

1. INTRODUCTION

There has been intense interest in recent years in studying inorganic nanomaterials, particularly rods, wires, dots, and related structures of II–VI semiconductors, because of the variety of possible applications.[1–3] Semiconducting nanoparticles show interesting optical, electronic, and other properties due to quantum confinement effects. Thus, it has been observed that the light emitted by CdSe quantum dots can be rendered polarized just by a change in the aspect ratio of the dots.[4] The quantum size effect in nanoparticles is strongly reflected in their Raman spectra as well. A reduction in the dimension of the crystallites leads to a shift and broadening of the first-order Raman line through a relaxation of the $q = 0$ selection rule. Raman spectroscopic studies of silicon nanoparticles were made by Richter et al.,[5] in which they explained the observed Raman spectra by the phonon confinement model (PCM). In this paper, we report Raman spectroscopic studies of CdSe nanotubes and ZnSe nanorods. Transmission electron microscopic studies of CdSe nanotubes and ZnS nanorods had suggested that these tubes and rods are made up of small spherical clusters. The main motivation for Raman measurements of these samples was to study confinement effects on optical phonons in the nanosized building blocks of nanotubes and nanorods.

2. EXPERIMENTAL DETAILS

CdSe and ZnSe samples were prepared by surfactant-assisted synthesis. For this purpose, Triton X-100 (t-octyl-C_6H_4-$(OCH_2CH_2)_xOH$) ($x = 9, 10$) was used as the surfactant.[6, 7] The synthetic procedure was as follows. A suspension of the respective oxide (10 mmol) was prepared with the use of Triton 100-X. To this, a solution of NaHSe (NaBH4/Se in 50 ml water) was added dropwise under inert conditions, refluxed for 12 h, and left overnight. The ratios of starting material to chalcogenide were 1:1. The product was washed with cyclohexane and diethyl ether and dried. A Triton 100-X concentration of 8–16 mmol generally yielded nanorods of the metal chalcogenides. A higher surfactant concentration of 24–40 mmol predominantly yielded nanotube-like structures in some cases. The ZnSe sample consists of rods, and the CdSe sample is a mixture of rods and tubes.

The samples were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD patterns were recorded with a Seifert instrument and CuK_α radiation with $\lambda = 1.5418$ Å. Conventional θ–θ plots were collected with a Bragg–Brenatano goniometer and a high-resolution, 169-eV Si(Li) solid-state detector with a 1 mm/2 mm slit. TEM images were obtained with a JEOL (JEM 3010) operating at an accelerating voltage of 300 kV.

Raman measurements were done at room temperature with a 5145-Å line from an argon ion laser and a micro-Raman setup in back-scattering geometry. The power on the sample was ~0.1 mW.

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