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Far-infrared Spectroscopy of a Nanocomposite of Polyvinyl Alcohol and Lead Sulfide Nanoparticles

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Abstract:

A nanocomposite consisting of lead sulfide (PbS) nanoparticles (NPs) with average diameter of 26 Å, according to absorption threshold shift, and polyvinyl alcohol (PVA) was characterized using far-infrared absorption spectroscopy. The experimental results are consistent with theoretical calculations that include proper mechanical boundary conditions at the nanocrystal-host interface.

Keywords: Nanoparticles, Far-infrared absorption, Two-phonon process.

Introduction

The usage of nanoparticles (NPs) as polymer fillers relates to the strong current interest in development and application of new materials [1, 2]. These, so-called, polymer nanocomposites combine size-dependent properties of NPs with desired properties of host polymers such as: possibility to be designed in various shapes, long-term stability and reprocessability. The resulting properties of nanocomposites are, most of the time, a simple combination of the properties of inorganic and organic components, although the appearance of completely novel characteristics sometimes can take place due to a synergistic effect.

Lead sulfide (PbS) is a narrow band gap semiconductor ($E_g = 0.41$ eV) with a large exciton Bohr radius (180 Å). Thus, when the crystallite size is smaller than the Bohr radius, a large blue shift of the absorption onset can be expected due to a size quantization effect. Since optical properties of PbS can be tuned into the spectral region important for many technology applications (1-2 μm) many methods have been developed to fabricate PbS NPs in micelles [3, 4], polymers [5-12], monolayer surfaces [13], zeolites [14, 15] and glasses [16].

Polyvinyl alcohol (PVA) is a hydrophilic polymer frequently used as a matrix for a variety of NPs [17-22]. In most cases, due to optical clarity, PVA has been used just as a host medium to enable investigation of optical properties of NPs. For example, femtosecond optical spectroscopy was applied to study the dynamics of excitons strongly confined in the PbS NPs incorporated in PVA films [21, 22].

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Synthesis and characterization

The synthesis procedure for the preparation of the PbS/PVA nanocomposite was already described elsewhere [23]. Briefly, 100 ml of 5×10^{-3} M $\text{Pb}(\text{NO}_3)_2$ solution containing 2.5 mass% of PVA was saturated with argon. 15 ml of H_2S was injected into the solution at room temperature and the solution was vigorously shaken for at least 5 min. Excess H_2S was removed by purging the solution with argon. In order to prepare PbS/PVA nanocomposites the solvent was evaporated at ambient conditions without the presence of light. The final concentration of PbS NPs in nanocomposite films was 4.6 mass%. Neat PVA films, without PbS NPs, were prepared in the same manner. All chemicals used were of the highest purity available (Merck or Fluka). Solutions were prepared using triply distilled water. Detailed information about structure analysis, thermal properties can be found elsewhere [23].

We determined the particle size from optical absorption spectra. The measurement was done by a VARIAN Super Scan 3 UV-VIS Spectrometre at room temperature. Pure PVA was used as the referent sample. The measured absorption spectrum of PbS QDs in a PVA matrix in the spectral region of 450 -700 nm is presented in Fig. 1. The blue shift compared to the bulk energy gap gives information about NPs dimension [24]. The average diameter is 26 Å.

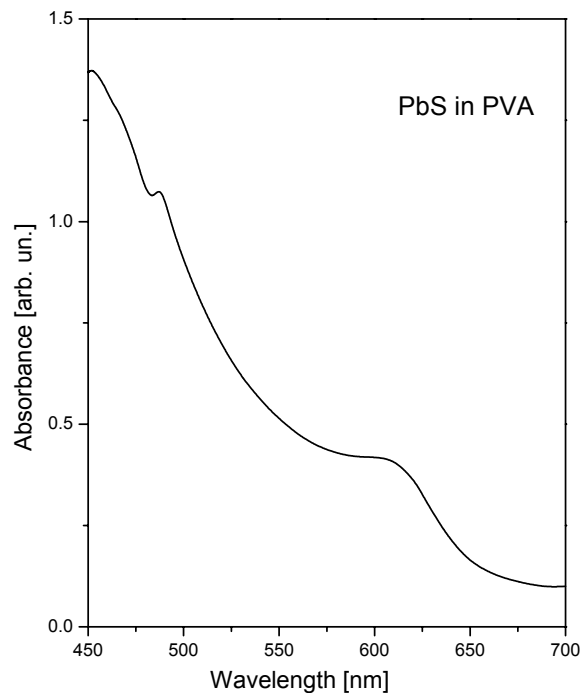


Fig. 1. Absorption spectrum of a nanocomposite of polyvinyl alcohol and PbS NPs with a diameter of 26 Å.

The far-infrared absorption spectra was measured at room temperature in the spectral range from 50 to 350 cm^{-1} , on a BOMEM spectrometer.

Results and discussion

The experimental FIR spectrum of the nanocomposite is shown in Fig.2. A broad

peak centered at $\sim 90 \text{ cm}^{-1}$ dominates the spectrum. There is also a smaller peak at about 275 cm^{-1} . The far infrared spectra of PVA were recorded to ensure that any observed features were not due to the host material.

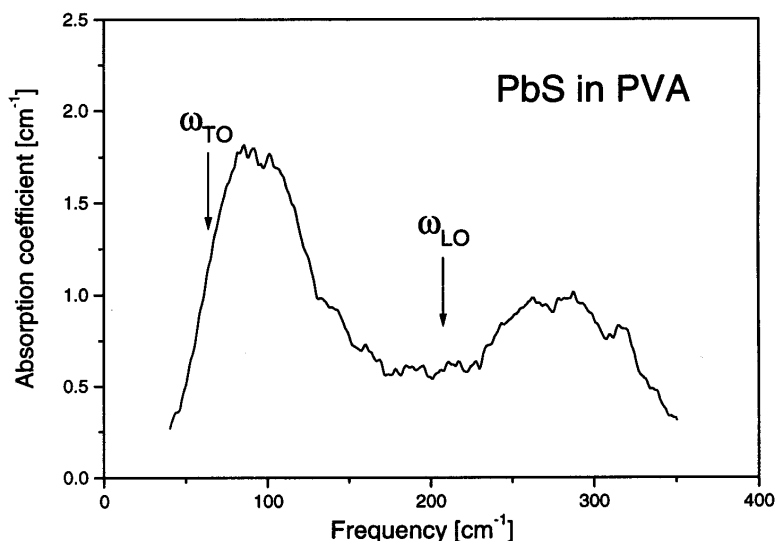


Fig. 2. Room temperature far-infrared absorption spectrum of a nanocomposite of polyvinyl alcohol and PbS NPs with a diameter of 26 \AA .

PbS is a IV-VI semiconductor, with a rock salt structure and a lattice constant $a_0 = 5.92 \text{ \AA}$. The optical phonons are very dispersive [25]. Longitudinal optic (LO) and transverse optic (TO) frequencies differ by a factor of 3 at the center of the Brillouin zone. In materials with dispersive phonons, phonon confinement can be obtained and studied easier. Phonon dispersion in PbS can not be modeled in the $\omega \sim q^2$ form and that unables an analytical solution. By adding a linear term, good fits to the measured dispersion curve can be obtained [25].

For an accurate treatment of materials with dispersive phonons, it is essential to satisfy the appropriate mechanical as well as electromagnetic boundary conditions. The theoretical framework given by Roca et al. [26, 27] can be applied to model small spheres of PbS embedded in a PVA matrix [28]. With an appropriate modeled phonon dispersion curve of PbS and the condition that the mode amplitude vanishes at the nanocrystal/host interface (it's reasonable because of the difference between structures) included in Roca's model, nanoparticle vibrational frequencies can be calculated.

The frequencies of calculated coupled modes depend strongly on spherical quantum numbers l_p and n , especially for small radii. Modes with $l_p = 1$ should be infrared active. In the limit of large radii for $l_p = 1$ and $n = 1, 2, \dots$, the TO components of coupled modes tend to the zone-center frequency $\omega_{TO} = 65 \text{ cm}^{-1}$ and LO components tend to $\omega_{LO} = 209 \text{ cm}^{-1}$. Closely spaced $l_p = 1$ solutions between 70 and 95 cm^{-1} form the band. The most interesting feature of this calculation are infrared active modes with frequencies far away from the zone center frequencies.

The broad peak in the far-infrared absorption spectrum with a peak at $\sim 90 \text{ cm}^{-1}$ can be attributed to coupled modes with $l_p = 1$. Many coupled mode solutions exist between 85 and 95 cm^{-1} , and these may contribute to the width of the peak. The agreement between the applied theory and experiment justifies importance of the assumed zero mechanical vibrational amplitude on the interface.

The experimentally registered band with a peak at $\sim 275 \text{ cm}^{-1}$ is above any lattice frequency [25] and above any nanoparticle frequency and cannot be attributed to one-phonon

processes. There is a peak in PbS NPs Raman spectra in the same spectral region [24, 28]. This band is assigned to a two-phonon process, and can be identified as a sum of frequencies of the $l_p = 0$ acoustic mode and $l_p = 0$ coupled optical mode.

Conclusion

Coupled optical phonon modes of nanocomposite of polyvinyl alcohol and PbS NPs have been observed using far-infrared absorption spectroscopy. The peak at about 90cm^{-1} is due to coupled modes with angular momentum $l_p = 1$. The broad peak at about 275cm^{-1} is above any lattice frequency and is close to the sum of the frequencies of the $l_p = 0$ acoustic and the $l_p = 0$ coupled optical mode (two-phonon process) of PbS nanoparticles.

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Садржај: Користећи далеку инфрацрвену апсорциону спектроскопију окарактерисан је композитни материјал који се састоји од олово-сулфидних честица окружен поливинил алкохолом. На основу померања апсорционог прага процењена средња вредност пречника честица је 26Å. Експериментални апсорциони спектри су у складу са теоријским прорачунима и усвојеним механичким условима на граничној површини честице.

Кључне речи: наночестице, далека инфрацрвена спектроскопија, двофононски процес.
