Quantum confinement effects on the phonons of PbTe quantum dots in tellurite glasses

G. J. Jacob, D. B. Almeida, W. M. Faustino, E. Rodrigues, C.H.Brito, L.C. Barbosa and C. L. Cesar
Universidade Estadual de Campinas
Instituto de Física Gleb Wataghin, P. O. Box 6165 CEP 13083-970, Campinas SP-Brasil.
gjjacob@ifi.unicamp.br

Abstract

We present Raman-scattering results for PbTe quantum dots (QDs) in doped telluride glasses which clearly show the confinement effects on the phonon spectra as a function of the quantum-dot size.

Introduction

Coherent acoustic phonons in PbSe semiconductors quantum dots in a polymer host have been observed in 1997 by Kraus and Wise (1) and in PbTe in borosilicate glass by our group in 1998 (2), both groups used femtosecond pump and probe experiments. Although Kraus & Wise have observed these phonons by both, pump and probe and Raman spectroscopy, we only observed them by pump and probe experiment. The direct pump and probe measurement in CdE [E = S, Se, Te] did not show these acoustic vibrations, that were only observed by photon echo experiments, although they have been observed by Raman spectroscopy. In a later publication (3) we did show that the degeneracy of the L bands of the Pb salts is responsible to allow this direct pump and probe observation of the breathing modes. The idea of the sequence for this phenomena is the following: (4) one photon excites one electron-hole pair, (5) like a free electron gas they exert pressure on the walls of the quantum dots, starting the breathing mode vibration on the picosecond time scale, (6) the size dependent electronic levels follows the particle size oscillation going in and out of resonance with the probe photon. (7), each oscillation of the quantum dots dissipates energy for host of the quantum dot bringing a strong damping time of the vibration. (8) both, the vibration frequency and damping time depend on the quantum dot size and the host parameters with the expression of the simplest model given by $\omega = {}^{2V}\!/_{R}$, where R is the quantum dot radius, and V the host sound velocity. However, a more complete model shows that the frequency depend on the transversal and longitudinal sound velocities and density of the host and the quantum dot.

Despite the fact that this is a general phenomena for all quantum dots, it does not imply that one will observe this oscillation of the probe beam absorption because the optical transition is Pauli blocked by the same electron-hole pair that trigger the oscillations. However, the degenerated electronic levels of lead salts still leaves unblocked levels that couples with the probe beam and the oscillations can be easily observed. These modes can be observed by Raman that do not depend on the electron transitions for the higher levels but only on the changes in the polarizability. These modes have also been observed by Raman in II-VI and InP quantum dots before, but they were observed only with photon echo with femtosecond experiment.

The effects of quantum confinement on the optical properties of quantum dots (QDs) in doped glasses have attracted attention because of the potential of these materials for optical-device applications due to their nonlinear optical properties [4-7]. Applications to light-emitting diodes [8-9] and laser mode locking [10] and the fabrication of novel superlattice structures [11], have already been demonstrated. IV–VI lead salt quantum dots are interesting for fundamental studies because their large Bohr radius allows for strong confinement with relatively large dots [12] and for applications because, with confinement, they can produce absorption at optical communication wavelengths [13-14]. The confinement effects on the electron and holes states, and their confined energy levels, have been extensively studied [15-20].

Despite the fact that we should have observed the coherent phonons by Raman we never have been able to do that before. Actually our attempts to observe even the LO PbTe phonon around 200 cm^{-1} was unsuccessful. For CdTe quantum dots in borosilicate glass we did observed quite strong LO phonon Raman lines at room temperature. With resonant Raman at low temperature we observed the surface optical SO modes and even some overtones and combinations of LO and SO modes. Using tellurite glass we did observed, for the first time, these acoustic phonons by Raman at low temperature with phonon frequency dependent on the quantum dot size. This is also the first time we have been able to observe the LO PbTe phonon, but only at low temperature.

Ultrafast Phenomena in Semiconductors and Nanostructure Materials XII
edited by Jin-Joo Song, Kong-Thon Tsen, Markus Betz, Abdulhakem Y. Elezzabi
Proc. of SPIE Vol. 6892, 689207, (2008) · 0277-786X/08/$18 · doi: 10.1117/12.761680

Experimental

Glasses preparation

The (50-25)TeO_2-(15-5)ZnO-(20-10)CdO-(15-5)B_2O_3-(30-10)BaO-(30-15)PbO (wt%) doped glasses were prepared by mixing tellurium oxide (TeO_2, 99.99%), zinc oxide (ZnO, 99.99%), barium oxide (Ba_2O_3, 99.99%), lead oxide (PbO, 99.99%), cadmium oxide (CdO, 99.99%) and boron oxide (B_2O_3 99.99%) and doped up to 15wt% PbTe (PbTe, 99.999% purity). This raw material was melted and homogenized at 950 ºC in an platinum crucible during 3 hours and quenched as rapid as possible by pouring it onto an inox steel plate, in order to avoid any initial QD growth and obtain clear glass sheets. A thermal annealing at 380 ^oC, very close to the glass transition temperature T_g, for 5 hours was done to diminish stresses. The QD nucleation happened at 400 ^oC for another 8 hours. The QD growth was done at 450 ^oC. To study the growth kinetics as a function of time 8 identical samples, in the form of 1 mm thick laminas, were removed from the furnace after 25, 27, 29, 31, 33, 35, 38 and 42 hours. Each sample was studied through the observation of the High Resolution Transmission Electronic Microscopy (HRTEM) and optical spectroscopy. The samples were prepared for HRTEM measurements by dimpling and ion milling and then crunched and diluted in isopropanolic alcohol. This solution was dripped into a NaCl crystal and, after NaCl dissolution in water and catched in a cooper net as a free standing quantum dot glass/carbon film. This film was analyzed in a JEOL 300 kV TEM operating at 300 kV. We checked the presence of Te and Pb by Electron Diffraction X-rays (EDX) and perform a Fourier transform on the digital micrographic photos to obtain the lattice parameters using the Digital Micrograph Software. The absorption spectra were taken with 1 mm thick samples by a Perkin Elmer λ9 spectrometer. The Raman-scattering measurements were performed with a dye laser and an argon laser as excitation sources and a Jobin–Yvon triple spectrometer (resolution 1 cm^{-1}) with multichannel detector. The spectra were obtained in a back-scattering geometry with the sample held in a close-cycle helium cryostat, where the temperature could be controlled from 10 to 300 K.

Results and discussion

Figure 1 shows the spectra for the eight different annealing thermal in the same samples telluride glass doped with PbTe QDs. They are similar to the PbTe QD in borosilicate glass spectra with the same red shift with time and the same absorption peak wavelength region, from 1000 to 2000 nm. The peaks have larger linewidth, however, suggesting these QDs present a higher QD size distribution than the borosilicate glass and in huge amounts.

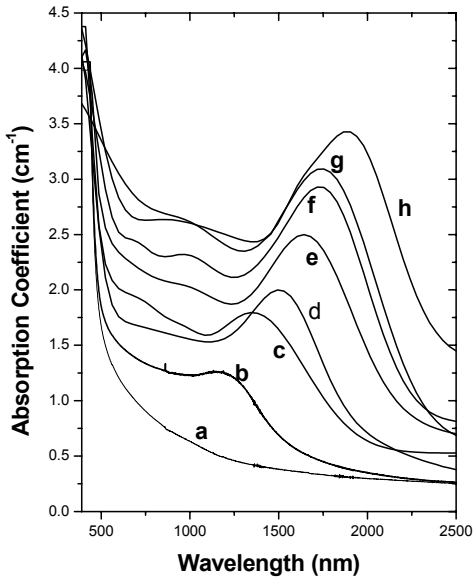

Figure 1. Absorption spectra from TeO2 glass PbTe QDs prepared at 450°C during: (a) as cast; (b) 25 h; (c) 27 h; (d) 29 h; (e) 31 h; (f) 35 h; (g) 38 h and (h) 42 h.

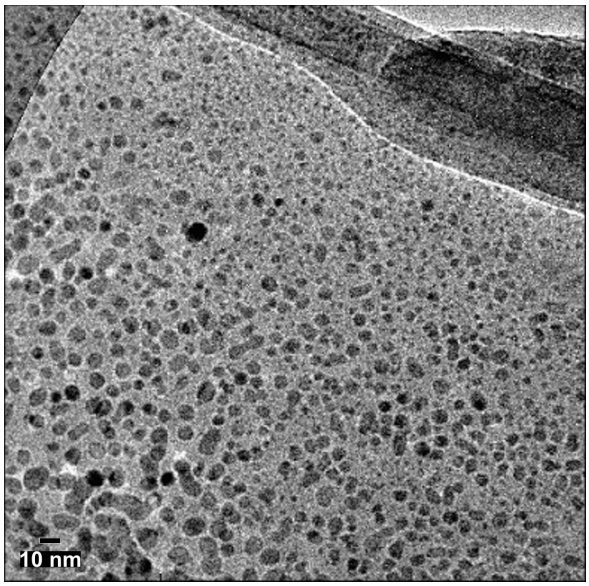

Figure 2. HRTEM microphotograph of a region with PbTe QDs in TeO2 glass treated for 38 h at 450°C

Figure 2 shows HRTEM microphotography of the QDs. It shows how dense the QDs are and gives an idea of the great size distribution and the great amount. The QDs volume corresponds to 30% of the total volume (14). Figure 3

show the Raman spectra from 50 to 250 cm^{-1} for temperatures varying from 300 to 17 K. Only below 155 K we started to observe the broad LO phonon at around 190 cm^{-1}, similar to the LO PbS QD phonon observed by Krauss et al (21). We attribute to the much higher solubility of PbTe quantum dots in tellurite glass than in borosilicate glasses the fact that we could not observe the LO phonons before. The concentration of QDs in the present sample is 10000 times larger than in the previous sample.

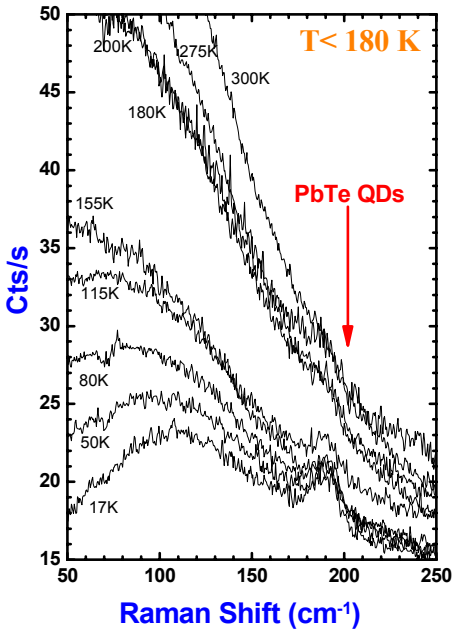

Figure 3: Raman shift to same telluride glass doped with PbTe QDs sample to 17 for 300K temperature range.

Figure 4 (a) show the 17 K spectra for the parallel and perpendicular polarization with respect to the incident beam, while figure 4 (b) show the 190 cm-1 peaks after subtracting the background and a 7 points smoothing. The glass scattering increases for the parallel polarization explain the enhanced background, but the peaks are essentially the same.

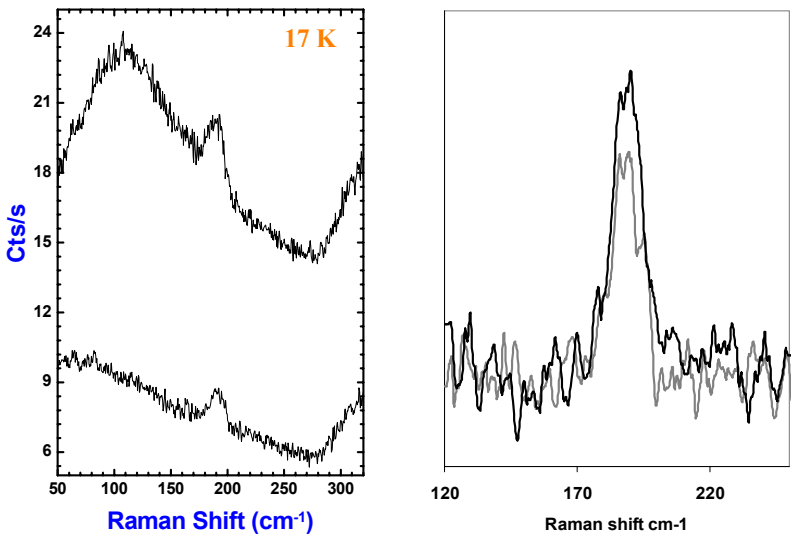

Figure 4: (a) Raman shift for parallel and perpendicular polarization. (b) Same peaks after background subtraction and 7 points smoothing.

Figure 5 shows the coherent acoustic phonon modes for three different samples. We can see the peak shifts from 40 to 42 cm^{-1}. The peaks of the coherent acoustic phonons changed from 39 to 43 cm-1. These values are comparable to the values obtained by Krauss and Wise (21) for PbS. Our previous pump&probe result varied from 18 to 22 cm-1 that suggests we are observing the overtone of the acoustic mode. We are further investigating the origin of the discrepancy between the pump & probe value and the Raman value. Again, we can explain the reason we could not see these acoustic phonon by Raman before due to the low concentration of QD in boroslilicate glasses. The pump & probe experiment is a differential experiment, sensible only to the population of excited quantum dots. Actually we could choose the size of the QD population excited just by changing the wavelength of the pump. Raman integrates over the number of particles inside the excited volume, including all QD sizes.

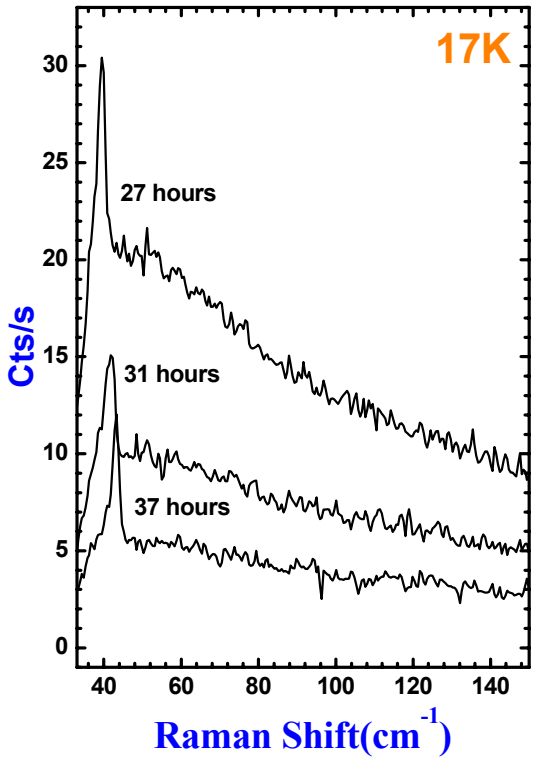

Figure 5: Raman scattering to samples doped with PbTe QDs showing shift with the size QDs.

Conclusion

In conclusion, we have clearly shown the size effects on the acoustic coherent phonon spectra of PbTe QDs at low temperature. We have been able to observe the LO phonon that was not possible before. The higher concentration of QD in Tellurite glass allowed our observation of both, the LO and the acoustical phonons. The value of the acoustic phonon frequency is close to previou PbS result but about twice of the pump&probe value we obtained before. We are still investigating this point.

References

1. Kraus and F. Wise;Phys. Rev. Lett. 79 (25), 5102-05 (1997).
2. E. R. Thoen et al, Appl, Phys. Lett. 73 (15) 2149 (1998)
3. Wise, F.; Acc. Chem. Res. 33, 773-780(2000).
4. S. Tsuda and C. H. B. Cruz, Opt. Lett. 16, 1596 (1991).
5. A. Nakamura, T. Tokizaki, H. Akiyama, and T. Kataoka, J. Lumin. 53, 105 (1992).
6. S. Ohtsuka, T. Koyama, K. Tsunetomo, H. Nagata, and S. Tanaka, Appl. Phys. Lett. 61, 2953 (1992).

7. K. Tsunetomo, S. Ohtsuka, T. Koyama, S. Tanaka, F. Sasaki, and S. Kobayashi, Nonlin. Opt. 13, 109 (1995).
8. V. L. Colvin, M. C. Schlamp, and A. P. Alivisatos, Nature ~London! 370, 354(1995).
9. Dabbousi, M. G. Bawendi, O. Onitsuka, and M. F. Rubner, Appl. Phys. Lett. 66, 1316(1995).
10. T. Guerreiro, S. Ten, N. F. Borrelli, J. Butty, G. E. Jabbour, and N. Peyghambarian, Appl. Phys. Lett. 71, 1595 (1997).
11. C. B. Murray, C. R. Kagan, and M. G. Bawendi, Science 270, 1335 (1995).
9. I. Kang and F. W. Wise, J. Opt. Soc. Am. B 14, 1632 (1997).
12. V. C. S. Reynoso, A. M. de Paula, R. F. Cuevas, J. A. Medeiros Neto, O. L. Alves, C. L. Cesar, and L. C. Barbosa, Electron. Lett. 31, 1013 (1995).
13. G.J.Jacob,C.L.Cesar,L.C.Barbosa, Chem.Phys.Glass 43C (2002)250 –252.
14. V. Esch, B. Fluegel, G. Khitrova, H. M. Gibbs, X. Jiajin, K. Kang, S. W. Koch, L. C. Liu, S. H. Risbud, and N. Peyghambarian, Phys. Rev. B42, 7450 (1990).
15. P. C. Sercel and K. J. Valhala, Phys. Rev. B42, 3690 (1990).
16. R. W. Schoenlein, D. M. Mittleman, J. J. Shiang, A. P. Alivisatos, and C. V. Shank, Phys. Rev. Lett. 70, 1014 (1993).
15. A. I. Ekimov, F. Hache, M. C. Schanne-Klein, D. Ricard, C. Flytzanis, I. A. Kudryavtsev, T. V. Yazeva, A. V. Rodina, and A. L. Efros, J. Opt. Soc. Am. B10, 100 (1993).
17. D. J. Norris, A. Sacra, and C. B. M. M. G. Bawendi, Phys. Rev. Lett. 72, 2612 (1994).
18. C. R. M. de Oliveira, A. M. de Paula, F. O. P. Filho, J. A. M. Neto, L. C. Barbosa, O. L. Alves, E. A. Menezes, J. M. M. Rios, H. L. Fragnito, C. H. B. Cruz, and C. L. Cesar, Appl. Phys. Lett. 66, 439 (1995).
19. R. Ruppin and R. Englman, Rep. Prog. Phys. 33, 149 (1970); R. Ruppin, J. Phys. C: 8, 1969 (1975).
20. E. R. Thoen, G. Steinmeyer, P. Langlois, E. P. Ippen, G. E. Tudury, C. H. Brito Cruz, L. C. Barbosa, and C. L. Cesar;Appl. Phys. Lett., 73(1998)
21. Krauss, T. D, Wise, F. W., Coherent and Acoustical Phonon in a Semiconductor Quantum Dots; Phis. Rev. Lett. 79, 5102-5105(1997).