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# Synthesis and optical properties of dense semiconductor–dielectric nanocomposites

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**Abstract.** We report on the Raman scattering spectra and fundamental absorption edge of dense semiconductor–insulator nanocomposites. These were synthesized by injection of the semiconducting melt into the channels of dielectric matrices. The Raman spectra exhibit shifts, broadenings, and asymmetries consistent with phonon confinement in nanometre-size semiconductor crystallites. Nanoscale networks of small effective mass semiconductors show evidence for electron confinement as manifested by a blue shift of the fundamental absorption edge.

As a result of finite size and surface effects, finely dispersed semiconductors display unusual physical properties such as an enhanced non-linear optical response which make them of current interest [1]. We have synthesized semiconductor–insulator nanocomposites in which the semiconducting phase occupies a significant (30%) volume fraction. This has been done by high pressure injection of the conducting melt into the nanometre-size channels of commercially available insulating matrices [2]. Small angle x-ray scattering measurements performed on composites synthesized from silica glass (porous Vycor) with interconnected 56 Å diameter pores show that the microstructure of the porous matrix is not modified by processing.

The structure of the semiconducting phase in semiconductor–porous-glass composites has been probed by x-ray diffraction and Raman scattering measurements. The x-ray diffraction spectra of Te– and GaSb–silica composites show that the semiconductors retain their bulk crystal structure and that they are not significantly strained ($\Delta a/a \leqslant 1.5 \times 10^{-3}$). From the width of the x-ray diffraction peaks a crystallite size $D$ of about 150 Å and 200 Å is obtained, respectively, i.e. larger than the 56 Å pore size of the matrix. Figure 1($a$) displays the Raman spectrum of the Te–silica composite and of a sample of single-crystal bulk Te. The strong $A_1$ optical mode of the composite exhibits a shift to higher frequencies and an asymmetric broadening. This is in contrast to the behaviour displayed by the modes of microcrystalline II–VI and III–V semiconductors (and apparently also the GaSb–Vycor composite), where low energy shifts are usually observed [3]. We interpret this as resulting from phonon localization in Te microcrystals of size $D$, by which the Raman process can occur via generation of phonons with momentum spread $\Delta q \approx D^{-1}$. Calculations based on the dispersion of the $A_1$ mode of trigonal Te, where energies increase rather than decrease away from $q = 0$, combined with the relaxation of wavevector selection rule for the excitation of the Raman active optical phonons in Te microcrystals about 150 Å in size yield shifts and broadenings consistent with the experimental data [4].

Preliminary evidence for electron localization in the nanocomposites based on GaSb, a small effective mass semiconductor, is obtained from a blue shift of the fundamental

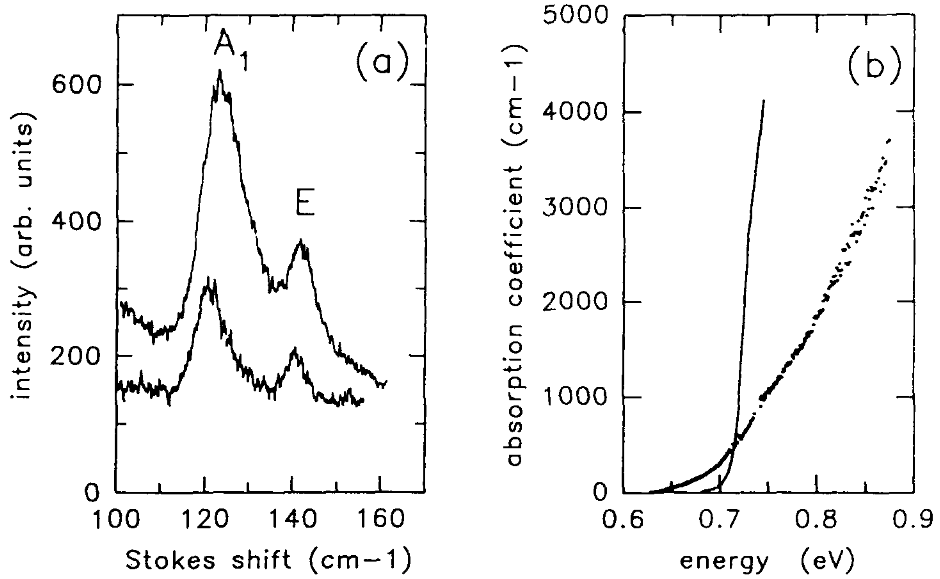


**Figure 1.** (*a*) Raman spectra of the Te–Vycor composite (top) and of bulk Te (bottom) at 300 K. (*b*) Room temperature absorption of the GaSb–Vycor composite (dots) and of bulk GaSb (solid line).

absorption edge as compared to that of bulk GaSb (figure 1(*b*)). The absence of a sharp, well-defined edge in the composite is likely due to a high density of defects and surface states.

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