Low-Frequency Raman Scattering in Materials Research

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The intention of this talk is to describe non-specialists with a basic understanding of the information low-frequency Raman Spectroscopy (LFRS) may provide when this characterization tool is applied to nanomaterials like oxide and semiconductor nanoparticles, nanoceramics and nanocomposite glassy materials. A short theoretical introduction of the Lamb theory on the vibrations of elastic spheres will be described for the free nanoparticles as well as for the nanoparticles embedded in matrix where the proper account on the boundary conditions should be taken.

The spherical case is well understood – the normal modes of the sphere are divided into torsional and spheroidal and, experimentally, have been measured in various situations, from very small structures like globular proteins or inorganic nanoparticles to very large structures like planets. Surprisingly the Lamb theory explains the observed results with reasonable agreement. The application of the Lamb theory will be illustrated by the LFRS measurements on different powder samples: TiO_2, SnO_2, ZnO and CdS. The effects of sintering of nanoparticles will be described with the ZrO_2 nanoparticles doped with Sn.

For the nanoparticles embedded in matrix a theoretical treatment of polarization-dependent low-frequency off-resonant Raman scattering which establishes a relation between the particle size, the frequencies, and the widths of various phonons, taking into account the matrix influence on the vibrational spectrum and on its damping, will be presented. In order to distinguish the confined acoustic phonons from the glass background, the spectra have been compared with those obtained from the base material, which does not contain nanoparticles. Polarized and depolarized scattering from confined acoustic phonons was distinctly resolved near the laser line and polarized inner particle modes were observed. The material-dependent generalized form of this analysis enables one to use it for any given combination of particle and matrix materials. A good agreement between the experimental and the theoretical results will be illustrated by TiO_2, CdS_xSe_{1-x}, and HfO_2 nanoparticles in glass matrix. The nanoparticle sizes and even sizes distribution obtained from Raman scattering agree well with those obtained from transmission electron microscope proving the LFRS to be a simple, fast and reliable method for the size distribution measurements. By inverse procedure, starting from the Raman spectra and known particles size distribution, the mean sound velocities of longitudinal and transverse phonons of nanoparticles could be deduced, providing LFRS to be unique technique for determination of the sound velocities in nanoparticles.

[1] H. Lamb, Proc. London Math. Soc. 13 (1882) 189.