

Preparation, Characterization, and Dynamical Properties of Nanostructured Metal-Oxide Materials.

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Objectives

The objectives of this NSF grant concerned the preparation, characterization and study of the static and dynamic optical properties of rare earth-doped insulating nanoparticles and nanostructured materials. New preparation techniques for preparing isolated and matrix-imbedded nanoparticles were to be examined. Samples were to be characterized using X-ray diffraction, electron diffraction, transmission-electron microscopy and atomic-force microscopy. Optical studies were to address issues of the location of the rare earth ions within the nanoparticles, comparison of the spectra with identical bulk materials, energy transfer both within the nanoparticle and between ions in different particles. Studies were to be performed on the effects of confinement on properties such as the radiative rate and quantum efficiency, homogeneous linewidth, and on changes in the dynamics of phonons.

We wish to point out that both laser and display industries can potentially take advantage of the tunability of optical and thermal properties provided by a doped nanoparticle/matrix composite. In particular an energy-efficient phosphor material that is unsuitable for computer or television screens due to a short persistence time might be tailored for these applications by preparing it at the nanoscale and embedding in an appropriate matrix.

Growth and Structural Properties

The $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ nanoparticles are prepared by gas-phase condensation using a cw- CO_2 laser to heat a ceramic target[1]. Material that vaporizes from the heated target forms gas-phase clusters that collect on a cold finger. The particle diameters are controlled between 25 to 4 nm by varying the vaporization conditions. Nanoparticles > 10 nm predominantly form in the metastable monoclinic phase. Nanoparticles < 10 nm contain multiple phases: monoclinic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, cubic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, monoclinic Eu_2O_3 , and a disordered phase. Annealing as-prepared 4 nm $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ at 500-900 C produces cubic-phase $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and removes all other phases. Grain growth depends on the anneal time and particle size can remain < 10 nm. Annealing as-prepared 13 nm $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ at 800-1000 C retains the monoclinic phase, showing that the crystal phase depends on preparation history and not only on annealing temperature.

Transmission electron microscopy (TEM) was used to determine the size distribution of the nanoparticles. The TEM data show that these nanoparticles form clusters. Both linear and nonlinear spectroscopic (holeburning) studies of both dilute ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$) and fully concentrated (Eu_2O_3) nanoparticles indicate that these particles possess an ordered structure when the nanoparticle diameter is > 8 nm, however the smallest nanoparticles ~ 5 nm appear to be disordered.

From the TEM results it is also clear that the nanoparticles deviate from a perfectly spherical geometry. While the elastic modes of spherical nanoparticles can be calculated analytically, this is not the case for nonspherical nanoparticles. We have used the approach of Visscher *et al.*[2] to explore how the mode structure becomes modified for ellipsoidal nanoparticles in which the spherical symmetry is broken[3]. The breaking of degeneracies due to the relaxation of spherical symmetry can impact the dynamical processes described below.

We have incorporated some of the larger nanoparticles in a polysilane matrix. While particles with a mean diameter of ~ 10 nm are too small to scatter light at optical frequencies we have been unable to satisfactorily disperse the nanoparticle clusters within the matrix with the result that the nanoparticle/polysilane matrix systems were highly scattering.

Dynamical Properties

We have achieved a number of important advances in our understanding of the dynamical properties of electronic states of ions in insulating nanoparticles. These include (1) the characterization and understanding of the effects of confinement on the electron-phonon interaction, (2) the demonstration of the interaction of ions within nanoparticles with the two-level systems of the amorphous matrix surrounding

the nanoparticles and (3) the observation and explanation for the dependence of the radiative lifetime on the matrix surrounding the rare earth-doped nanoparticles.

Confinement effects on the electron-phonon interaction

One phonon relaxation processes in nanocrystals: Crystal field split electronic states of rare earth ions are usually coupled by the continuum of phonons whose energies are resonant with the energy gaps between these states and whose density of states increases quadratically with frequency. In nanoparticles there is a gap in the density of states and the low frequency modes form a discrete spectrum. As a result it is expected that low energy electronic transitions will not necessarily be resonant with a nanoparticle mode. Electronic relaxation processes in nanoparticles are therefore expected to be modified when compared to their bulk material counterparts.

We have investigated this in an electronic triplet of monoclinic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanoparticles which has electronic states separated by 3 cm^{-1} and 4 cm^{-1} . Fluorescence transients of Eu^{3+} transitions between components of the $^5\text{D}_1$ and the $^7\text{F}_3$ manifolds were found to exhibit a slow relaxation in nanoparticles compared to transients measured on the same transitions in micron scale materials[4]. These results are interpreted as an inhibition of the one phonon emission decay process caused by modification of phonon density of states due to the finite size of the nanoparticle. The residual relaxation is attributed to coupling of the nanoparticle with other nanoparticles in the cluster. Modes of the nanoparticle cluster can influence the one phonon emission either directly by coupling to the electronic states or indirectly by broadening the nanoparticle modes[5].

Line shapes in nanocrystals: Bimodal transient luminescent lineshapes have been reported in $\text{ZnS}:\text{Mn}^{2+}$ nanocrystals embedded in a polymer (polyvinyl butyral) matrix. After intense laser excitation, the time resolved fluorescence was observed to form two emission bands that merge into one as time progressed[6]. We have calculated fluorescence lineshapes as a function of time by assuming a nonequilibrium initial phonon distribution for the excited vibronic states coupled to a reservoir of lattice modes at room temperature. Our calculation was able to reproduce the experimentally observed lineshapes and enabled us to extract a value of the coupling constant of $5 \times 10^4\text{ s}^{-1}$ [7].

New mechanisms for electronic energy relaxation: As a result of the nonradiative relaxation experiments described above, we have proposed a novel nonradiative relaxation mechanism caused by inertial coupling of an electron to the center of mass motion of a nanoparticle[8]. This mechanism is operative even at zero temperature and is expected to occur with a rate of 10^2 - 10^3 s^{-1} depending on the details of the cluster. It should be pointed out that while this mechanism is too slow to account for the residual nonradiative relaxation observed above, it should be possible to observe this mechanism in the ground state manifold of a rare earth ion by means of an infrared quantum counter experiment.

Two-phonon Raman scattering: For isolated electronic states where the direct process is not active, two-phonon Raman scattering often dominates relaxation and determines the optical dephasing or homogeneous linewidth. In bulk materials this is weak and exhibits a T^7 temperature behavior. Because of the modified phonon density of states in nanoparticles due to confinement effects, it is expected that this temperature dependence will be altered and that a particle size-dependence will appear. We have carefully characterized this behavior by studying particles of different size distributions and find that for the nanoparticles (a) the dephasing rates are strongly enhanced, (b) the temperature dependence becomes a T^3 behavior at low temperatures and (c) a size dependence of the dephasing rate appears which is $1/d^2$ where d is the particle diameter[9]. We have performed calculations of the confinement effects on the two-phonon Raman scattering that successfully describe the experimental findings. The calculations take into account the effect of size confinement on the phonon wave function amplitudes, the actual phonon frequency spectrum of a spherical particle[10] and the two-phonon Raman rate of the bulk material. The best fit to the data require that the discrete phonon resonances of the nanoparticle broaden as the square of the phonon frequency and that the phonon dephasing times are about 40 ns for 25 cm^{-1} phonons. This represents the first evidence about the lifetime of these phonon modes.

Interactions of ions in nanoparticles with excitations of an amorphous matrix

The homogeneous linewidths of electronic transitions of Eu^{3+} and Pr^{3+} rare earth impurity ions in Y_2O_3 and LaF_3 nanocrystals embedded into amorphous materials (polymer and oxyfluoride glass ceramics) were studied with hole-burning and fluorescence line narrowing techniques. We have shown that the low-temperature homogeneous broadening is determined by the interaction of the ions with the two-level systems of the matrix. This provides a direct confirmation of the relatively long-range ($>10\text{ nm}$) character

of impurity ion-TLS interaction. The embedded doped nanocrystals thus may serve as a probe of glass dynamics. The advantage compared to ions directly embedded in glass is the sharp-line spectra and the possibility to exclude (if necessary) the effects caused by short-range interactions with very near TLS in glass. Embedding rare-earth ions into nanocrystals of different sizes provides the unique possibility to vary the homogeneous width of electron transitions.

Modification of Radiative Lifetimes

The prospect of modifying the radiative rate of ions in solids is an important goal in developing materials for applications. The use of various optical cavities is one means to carry out this objective. We have demonstrated that the radiative rate of ions imbedded in nanoparticles can be controlled by placing the particles in matrices with different indices of refraction[11]. In the case of Y_2O_3 nanoparticles containing Eu^{3+} , the radiative rate was increased by a factor of four by placing the particles in liquids of various indices of refraction. The cause of this effect is the combined action of the surrounding medium on the density of photon states and on the local field acting on the radiating center, since both of these properties are dependent on the effective index of refraction of the nanoparticle and its surrounding environment, averaged over a length scale corresponding to the wavelength of light. It is important to recognize that in this case, the modifications of the radiative rates occur with no change in the optical spectrum since the local environment of the optical center is unaffected by the changes in the medium surrounding the nanoparticle, in contrast to other examples where the local environment is used to modify the effective index of refraction.

Future Challenges

The major challenge that we foresee in the near future will be the incorporation of dispersed nanoparticles in a matrix and the acquiring of a detailed understanding of the interactions between ions within the nanoparticles and excitations of the matrix. This advance is an important step in developing optical quality nanocrystal based materials. Optical quality materials in addition to being of import to the laser and display industries are also essential for the success of nonlinear spectroscopic techniques.

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*For additional information visit: <http://www.chem.vt.edu/chem-dept/tissue/nano/>

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