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CdS_xSe_{1-x} NANOCRYSTALLITES: NEW MATERIALS FOR NON LINEAR OPTICS

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Abstract - Nanocrystallites of CdS_xSe_{1-x} semiconductors in glasses have non-linear properties which are function of the exciton confinement due to their sizes. The determination of the diameter of these nanocrystallites, critical to improve the properties of the systems, is determined by Raman scattering close to the laser line: the Low Frequency Inelastic Scattering (LOFIS). Possibility to determine the size distribution by LOFIS is demonstrated and effects of thermal treatments on the sizes and the size distribution of is discussed.

1- INTRODUCTION

Mesoscopic systems, intermediate between the bulk material and the molecule, attracted recently much interest both from a fundamental point of view and for their potential applications for non-linear optics. Among them CdS_xSe_{1-x} semiconductors in glasses are widely studied: nanocrystals with diameters smaller than the Bohr diameter of the exciton can be grown in the glassy matrix. Quantum confinement effects are then expected and non-linear optical properties are observed in these systems. Optical properties of II-VI semiconductors nanocrystallites are known for many years as optical filter, the absorption edge being function of the sulfur content x. From the precursor of these filters nanocrystals with different sizes are easily obtained by controlled heat treatments. In this paper we will present briefly non-linear optical properties and focus then on a critical point for their improvement: the size distribution of the nanocrystals in the glass.

II QUANTUM SIZE EFFECTS:

The more direct evidence of quantum size effects in the CdS_xSe_{1-x} semiconductor doped glass is given by their absorption spectra. On the figure 1 this absorption is shown at low temperature (10 K) for a given concentration x=0.9 as function as the diameter of the particles. The shift of the absorption band is explained by quantum confinement effects: the diameter of the nanocrystals being of the same order of magnitude than the Bohr radius of the exciton.

This type of material is usually described as "Quantum dots". In the crystals of larger dimensions (10 nm) the absorptive and refractive non-linearity has been measured. The \( \chi^3 \) value (10^{-9} esu) is smaller than in multiple quantum wells but the fast recovery times (10ps) and the possibility to increase the \( \chi^3 \) by confinement effects make this field very active.

The absorption edge of the nanocrystallites absorption is dominated by the first excitonic absorption, the position of which has been first described by the effective mass approximation /1/. The tight binding approximaton developped recently /3/ gives however a better quantitative agreement with the experiments /4/.

On the figure 1 the particles size is determined by Low Frequency Raman Scattering (LOFIS). This method, based on Raman scattering close to the Rayleigh line, was recently applied to this type of materials /5/. The energy of the low frequency peaks \( \omega \) is expressed as:

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a being the radius of the nanocrystallites and $S$ a factor taking into account the sound velocity, the shape of the particles and the modes of vibration interacting with the light.

A good correlation between the results obtain by LOFIS and High Resolution Electron Microscopy or Small Angle X-Rays scattering is established [6]. A goal to improve the non-linearity of these materials is to reduce the width of the emission lines [7]. One of the possible reason for the inhomogeneous broadening is the size distribution that we will now discuss using the experimental results given by LOFIS.

III SIZE OF NANOCRYSTALLITES.

The nanocrystallites on the figure 1 are grown from the glassy matrix by heat treatment at 650°C for several hours. The nucleation and growth process of crystals in glasses are extensively studied for the production of glassceramics [8]. The Ostwald ripening described the growth of the larger particles to the detriment of the smaller. The critical radius is then defined as the radius of the particle in a stationary state and it can be shown [9] that it corresponds in this theory to the mean radius of the population. The theory of the diffusion limited growth [9] leads to:

$$a^3 - a_0^3 = k \tau$$

Experimentally it is possible to test the validity of the expression (2). The figure 2 is a plot of $a^3$ as function of the time $\tau$ in hours. The agreement with (2) is observed which means that the diffusion limited growth is most probably the mechanism governing the growth of the crystallites. This conclusion, established for a radius of particles a larger than 2.5 nm, cannot be extended to any nanocrystallites, the Ostwald ripening being only the second stage of the nucleation-growth process.

One way to improve the non-linear properties of this type of material is the reduction of size distribution. Very sharp exciton-absorption peaks are obtained for monodisperse 1 nm clusters [3] and high fluorescence quantum yields at room temperature are measured for highly monodisperse CdS particles [10].

It is well known in the case of glass-ceramics that ultrafine crystallizations can be obtained with a two stage heat-treatments producing first a large number of nuclei [11]. This process can be used also for semiconductors doped glasses.
DISCUSSION AND CONCLUSION:

The reduction of the emission line width is certainly a decisive point to determine if CdS$_x$Se$_{1-x}$ quantum dots are good candidates for non-linear applications. Both homogeneous and inhomogeneous line width are observed. Homogeneous broadening has been observed at room temperature and its origin is controversial. Phonon broadening has been proposed as a possible mechanism whereas a quantization of the hole motion could be proposed. The inhomogeneous broadening is as shown in very important.

The diffusion limited growth postulated experimentally implies theoretically a size distribution $f(z)$ very asymmetric with a tail extending very far for small sizes (fig 3). This point has however to be corrected if we consider the interaction with light as in this case the volume fraction is more pertinent to describe the absorption. The fact to consider the volume distribution rather than the number of particles favours the contribution of the large particles and the actual distribution to consider is more narrow than on the figure 4. Improvement of the inhomogeneous broadening can be expected by using different types of thermal treatments specially to produce very small nuclei where strong confinements effects are expected. Alternative ways to produce CdS$_x$Se$_{1-x}$ particles by the sol-gel route or clusters by chemical reactions are also very active.

Fig 3. Particle size distribution for a diffusion limited process (from /9/).

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