Optical investigation of microcrystals in glasses

M.Ferrara,M.Lugarà,C.Moro+
R.Cingolani,C.De Blasi,D.Manno++
G.C.Righini+++

+ Dip. di Fisica - Univ. di Bari (Italy)

++ Dip. di Scienze dei Materiali - Univ. di Lecce (Italy)

+++ GNEQP and IROE/CNR - Firenze (Italy)

ABSTRACT

We have studied $\text{CdS}(x)\text{Se}(1-x)$ semiconductor doped glasses by means of optical techniques such as absorption, emission and Raman spectroscopy, in order to put in evidence the low dimensionality and quantization effects associated with the presence of $\text{CdS}(x)\text{Se}(1-x)$ microcrystallites in the glass matrix. By applying simple models to our experimental results it is possible from either absorption and luminescence or Raman spectra to calculate the effective dimension of microcrystals; these values very well agree with transmission electron microscopy data.

Moreover by using a pump and probe technique, we have studied the absorption changes in $\text{CdS}(x)\text{Se}(1-x)$ microcrystallites, resulting in the shift of the absorption edge and in the bleaching of the excitonic resonance, when the pump intensity is increased.

1. INTRODUCTION.

Coloured glass filters containing binary or ternary semiconductor microcrystallites are widely studied not only from the fundamental point of view, since they show low dimensional features, i.e., a quantum dots like behaviour of microcrystallites, but also for their possible practical applications in non linear optics as high speed bistable or switching devices, saturable absorbers, etc. .

The optical absorption edge of glass filters is controlled not only by the nature and the composition of the doping semiconductor, but also, and strongly, by the temperature and the duration of the thermal cycles to which the glasses are exposed in order to obtain the desired colour. Indeed the thermal cycling strongly affects the dimension of semiconductor grains in the glass matrix. A spherical shape can be assumed for such microcrystallites, as confirmed by their direct observation with the Transmission Electron Microscope (TEM).

The mean radius of microcrystals, as compared with the Bohr radius of the exciton in the doping semiconductor, is the main parameter governing the optical non-linearities in glasses. The aim of our

work is the study of microcrystals in glasses by means of non-destructive optical techniques. We have investigated coloured glass filters doped with $\text{CdS}(x)\text{Se}(1-x)$. Optical absorption and photoluminescence measurements have been performed in order to put in evidence quantization effects and, on their basis, to calculate the mean radius of microcrystallites. Raman spectroscopy has been also carried out, allowing us to evaluate, independently of luminescence experiments, the mean composition and the mean radius of the semiconductor grains in the glass matrix. The non-linear behaviour, i.e., the intensity dependent absorption changes, has been studied by means of the "pump and probe" technique, performed with nanosecond pulsed optical sources.

2. RESULTS AND DISCUSSION.

Absorption and photoluminescence spectra of doped glasses have been measured in the temperature range between 10 and 300 K. The excitation source for photoluminescence was the second harmonic of a Nd:YAG laser, with a pulse duration of about 10 ns and a peak power of 15 MW at 532 nm. Both absorption and photoluminescence put in evidence the excitonic transitions associated to the quantized subbands of microcrystallites. In fig.1 we report the absorption and photoluminescence spectra at 10 K of two samples, i.e., OA83A and KS19D, containing $\text{CdS}(x)\text{Se}(1-x)$, with a nominal x in the doping powder of OA83A more than five times that of KS19D.

Fig.1 Absorption and photoluminescence spectra at 10K of OA83A (left) and KS19D (right). LEI-PL and HEI-PL mean 1.4 KW/cm^2 and 140 KW/cm^2 excitation intensity photoluminescence, respectively.

First level excitonic transitions are well put in evidence for microcrystallites in both glasses either by absorption or by low excitation intensity photoluminescence, as shown in fig.1 for OA83A. The positions in energy of the absorption edge allow us to estimate x values in $\text{CdS}(x)\text{Se}(1-x)$ of 0.5 and 0.1 for OA83A and KS19D, respectively. When the excitation intensity strongly grows, photoluminescence spectra show the rising of a new emission on the high energy side, due to the filling of the first excitonic level of the subband. A clear evidence of such behaviour is reported in fig.1 for both OA83A and KS19D. The separation in energy between the two emission peaks, corresponding to that between the first two excitonic levels, is strongly dependent on the mean radius of microcrystallites. This dependence is described by a simple model that gives¹

$$\Delta E = (0.71 \hbar^2 / 2 m_e R^2) (\phi_{2,m}^2 - \phi_{1,m}^2) \quad (1)$$

where m_e is the effective mass of electrons and $\phi_{2,m}$ and $\phi_{1,m}$ are the roots of the Bessel functions.

From our experimental data, by means of the above formula, we obtain $R=60 \text{ \AA}$ for OA83A and $R=70 \text{ \AA}$ for KS19D.

In the Raman spectra of semiconductor microcrystallites in glass matrix the scattering due to surface modes appears on the low energy shoulder of bulk-like phonon lines of the semiconductor. In fig.2 the Raman spectra of OA83A and KS19D samples, obtained at 80 K under 50 mW excitation at 514.5 nm, are reported.

Fig.2 Raman spectra at 80K of OA83A and KS19D glasses under 50 mW argon laser excitation at 514.5 nm. The arrow marks the position of LO mode of bulk CdSe.

For both glasses there is evidence of surface phonon scattering. From the ratio between the total CdS-like and CdSe-like scatterings we can approximately estimate x values of CdS(x)Se(1-x) ranging from 0.5 to 0.6 for OA83A and from 0.1 to 0.2 for KS19D. Moreover, since the relative scattering intensity of surface phonons, compared with the bulk modes, is a decreasing function of the radius of microcrystallites, by means of a theoretical model² it is possible to evaluate the mean radius R of the grains of CdS(x)Se(1-x) in our glasses from Raman data. We find R values ranging from 2 to 5 nm in OA83A and from 10 to 40 nm in KS19D.

The Transmission Electron Microscopy measurements, performed on chemically thinned specimens by means of a Philips 400T microscope, operating at a 120 kV accelerating voltage, confirm the values we have found for the mean radius of microcrystallites by means of our non-destructive techniques.

Table 1 summarizes the experimental values of x and R obtained with the above measurements.

SAMPLE	R(Å)			X	
	PL	Raman	TEM	ABS	Raman
OA83A	60	20-50	25-100 500	.5	.6
KS19D	70	130-140	20-60 120-400	.1	.1
OS11C	-	30-75	20-60	.9	.8
KS17D	-	100-170	20-60 170-600	-	.2

Table 1. Experimental values of x and R obtained with different spectroscopic techniques.

In glasses containing microcrystallites whose radius is comparable with the Bohr radius of exciton in the doping semiconductor a non linear behaviour of the absorption, as a consequence of the quantization effects, is expected when the excitation intensity is increased. In fig.3 the transmission spectra of OA83A glass at RT are reported for different excitation intensities from a broad pulsed dye laser, ranging from 0.1 to 1 kW/cm². The shift of the absorption edge when excitation power increases is evident and can be easily ascribed to a band filling effect.

Fig.3 Transmission spectra of OA83A glass at RT for different values of incident intensity from a broad band pulsed dye laser ($I_0=1 \text{ KW/cm}^2$) .

Fig. 4 shows the results of the measurements performed with the "pump and probe" technique on the same OA83A glass at RT. The "probe" source was a broad dye laser peaked at 580 nm, whereas the second harmonic of a Nd:YAG laser, with an intensity variable between $0.2 I_0$ and $I_0 = 0.56 \text{ MW/cm}^2$, was used as "pump". The variations in the absorption near the excitonic transitions, associated to a progressive bleaching of the exciton induced by the "pump" beam, are shown as the absorption changes $L \cdot \Delta\alpha$. As clearly appears in fig.4, the effect is worth and supports the idea of using doped glasses as optically controlled light switches.

Fig.4 $L \cdot \Delta\alpha$, i.e., the absorption changes as a function of the wavelength of the "probe" source and for different values of the "pump" intensity ($I_0 = 0.56 \text{ MW/cm}^2$).

3. CONCLUSIONS.

Optical spectroscopy techniques have been shown to be able to determine with a good approximation the mean composition and the mean radius of microcrystallites of ternary doping semiconductors in glasses without need of destructive analytical measurements or TEM

observations. Optical tests are also useful to put in evidence the non-linear properties of glasses, that strongly depend on the thermal cycling also. More effort must be produced in order to make deterministic the correlation between the glass treatment and the properties of microcrystallites.

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