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$\text{CdS}_x\text{Se}_{1-x}$ nanocrystals in a silicate glass

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Abstract

A dilute system of $\text{CdS}_x\text{Se}_{1-x}$ nanocrystals with low anisotropy and low size dispersion has been studied by SAXS. The presence of angularities at the surface of the nanoparticles is evidenced from the limit at zero of the chord distribution function. Moreover in a model of spherical particles the size given by the average chord does not agree with that given by the integral parameters. A cubic particle shape has been used to evaluation of the size distribution. This distribution agrees with the expected one, and allows to confirm the validity of a polyedral model for the treatment of the SAXS data. Structural information on the particle surface can be deduced from the presence of the angularities.

Introduction

In $\text{CdS}_x\text{Se}_{1-x}$ doped glasses the crystal sizes are of the same order of magnitude than the radius of the exciton. Quantum confinement effects are then expected and observed. The influence of the size on the excitonic, optic and electronic properties of the material has given rise to a large number of studies. It has been observed that other structural parameters (as the surface and the structural defects) may affect the optical response of the nanoparticles. Since a few years many groups have dealt with a better structural knowledge of the nanoparticles. The kinetic of the growth has been studied by TEM, HRTEM and SAXS. HRTEM studies have been used to get information on the structure of the nanocrystals. For nanoparticles with size of the order of 50 Å it has been observed that the shape is nearly isotropic and that the size distribution is low [1].

The results given by different methods have also been compared. It has been observed that the sizes measured by HRTEM are significantly lower than those measured by SAXS. Moreover domains of absorption contrast extending outside the lattice images in HRTEM studies have been observed. This suggests the presence of a domain of "intermediate" order at the surface of the nanoparticles, ie amorphous or misoriented with respect to the monocrystalline kern. It is then of a great interest to get further information about the surface of the particles.

The use of SAXS data to get information about nanostructures is well developed. The theoretical methods for the evaluation of structural parameters in a dilute system containing identical monodisperse particles are well known, however the problem of the SAXS study of non monodisperse dilute systems has been often attacked and is still open. The great deal is how to get separately information about the shape and the polydispersion of the particles. It has been shown by Mering and Tchoubar [2] that a clear distinction between smooth and angular particles can be made from the study of the asymptotic behaviour of the scattering curve in range of high q .

Several studies have been devoted to the determination of the size distribution for polydispersed systems of spherical particles. The particles angularities are not taken into account in these descriptions. In most case one must count oneself lucky to have a general characterization of size polydispersity and shape. The main reason is the great loss of information due to averaging a polydisperse system of non isotropic particles.

In the system studied here the $\text{CdS}_x\text{Se}_{1-x}$ nanocrystals embedded in a the glass matrix are known to be nearly isotropic and to have a narrow size distribution. It can therefore be expected that some information about the particle shape can be separated from the information about size dispersion. The present study is an attempt to get this information.

Chord distribution and particle angularities

The chord distribution is an useful description of a multiphase medium. It has been shown [3] that this description can be used to detect angularities at the surface of particles. If straight lines are assumed to pass through a volume containing particles, in every direction and everywhere, one defines the chord distribution function $G(x)$ by the probability $G(x)dx$ for one line to intersect a particle by a segment of length x . $G(x)$ satisfy the normalisation condition: $\int_0^\infty G(x)dx = 1$. The chord distribution function is related to the correlation function $\gamma(r)$: $\gamma''(r) = -(2/rd)\delta(0) + (1/rd)G(r)$
 rd is the first moment of the chord distribution $rd = \int xG(x)dx$.

The evaluation of the limit of $G(r)$ for $r \rightarrow 0$ is especially useful. This limit is related to the angularities on particles surfaces [3, 4]. If the particles are round shaped $G(0)=0$, if the particles present some angularities $G(0) \neq 0$. An experimental determination of this limit is obtained from the difference of areas above and below the asymptote in a Porod plot $q^4 I(q) = f(q)$. This experimental determination is limited by the range of validity of the asymptotic behaviour ($q < q_b$, q_b limit of the Brillouin zone for the nanoparticles) and the low signal over noise ratio in the high- q domain.

Characteristic parameters and particle shape

The characteristic parameters obtained from the SAXS curves can be separated in so called "differential" and "integral" parameters [5]. The integral parameters are obtained from integral of the correlation function $\gamma(r)$. The most useful are: the radius of gyration r_g , the coherence surface fc , the coherence volume vc and the coherence length τ_l [6, 7].

$$fc = \tau_l^2 = \int_0^\infty 2\pi r \gamma(r) dr \quad vc = \tau_l^3 = \int_0^\infty 4\pi r^2 \gamma(r) dr$$

$$\tau_l = 2 \int_0^\infty \gamma(r) dr \quad r_g^2 = (1/v) \int_0^\infty 4\pi r^4 \gamma(r) dr$$

The differential parameters correspond to the first, second, etc... derivatives of $\gamma(r)$. The average chord rd is a differential parameter: $r_d = -1/(\gamma'(r))_{r=0}$. Porod [5] points out that these parameters determine the course of the correlation function at small distances that means near the particle and give some information regarding the structure surface. It is then expected that whereas the integral parameters only contain information about the particle size, the differential parameter r_d can a priori be used to distinguish between different particle shapes.

For a system of monodisperse particles with the same shape and uniform density the particles are characterized by only one linear size parameter S . For a given shape one can define a set of coefficients $\alpha_g, \alpha_d, \alpha_v, \alpha_l$, and α_f corresponding to the values of the linear lengths r_g, r_l, r_v, r_l , and r_d deduced from the characteristic parameters for a reference particle with size parameter $S=1$. These coefficients relate the characteristic parameters to the size S [8, 9]:

$$\alpha_f S = r_f; \quad \alpha_l S = r_l; \quad \alpha_v S = r_v; \quad \alpha_d S = r_d; \quad \alpha_g S = r_g$$

For a sample composed of particles with different sizes but the same shape the size distribution function $F(S)$ is defined such that $F(S)dS$ is the fraction of particles having a size parameter between S and $S+dS$. $F(S)$ is thus normalized such as $\int F(S)dS = 1$. In that case the linear size S_i deduced from the characteristic parameters correspond to average values involving different ratios of the n th moments of the size distribution function. It has been shown [5, 10] that:

$$S_d = \langle S^3 \rangle / \langle S^2 \rangle; \quad S_l = \langle S^4 \rangle / \langle S^3 \rangle; \quad S_f^2 = \langle S^5 \rangle / \langle S^3 \rangle; \quad S_g^2 = \langle S^8 \rangle / \langle S^6 \rangle; \quad S_v^3 = \langle S^6 \rangle / \langle S^3 \rangle$$

$$\text{with } \langle S^n \rangle = \int S^n F(S) dS.$$

An information about the size dispersion can then be obtained by comparing the sizes S_i deduced from the different characteristic parameters:

$$\alpha_f S_f = r_f; \quad \alpha_l S_l = r_l; \quad \alpha_v S_v = r_v; \quad \alpha_d S_d = r_d; \quad \alpha_g S_g = r_g$$

Samples and data treatment

The glass studied was prepared by the Schott Glaswerke and has a composition close to that of the commercial filters RG630 (around SiO_2 46%, K_2O 20%, ZnO 21%, TiO_2 6%, B_2O_3 4%, in weight % of each oxide). The total amount of the colouring elements Cd, S and Se does not exceed 1% in weight. The nanocrystals are obtained by an heat treatment of 2 hours at $T = 590^\circ\text{C}$. The thickness of the sample is $120\mu\text{m}$. The sample was carefully polished with 0.5mm diamond paste to avoid any superimposed scattering due to surface effects.

The SAXS measurements have been performed using a RIGAKU rotating anode working with a powder of 5kW. The X-ray beam of wavenlength $1.5405\text{\AA}$ ($\text{CuK}\alpha_1$) was focused in the detector plane by a curved Ge111 monochromator. Point-like slit conditions with an irradiated cross section of about $0.4 \times 1\text{mm}^2$ were used. The intensity for each value of q is proportional to the counting rates of a gas detector. In order to get a statistic error of less than 5% even in the high q domain the acquisition time is 60 hours. The scattering curve were obtained in the range of scattering vector amplitude ($q = 4\pi \sin\theta/\lambda$) $q_{\min} = 0.510 \cdot 10^{-3} \text{\AA}^{-1}$ to $q_{\max} = 0.5 \text{\AA}^{-1}$, with $\delta q = 10^{-3} \text{\AA}^{-1}$.

figure 1 : different steps for the data treatment.

The second step is to obtain normalized data. A plot $\ln(I)=f(q^2)$ is performed. A linear regression between $q^2=510^{-5}$ and $q^2=5 \cdot 10^{-3}$ gives a radius of gyration $R_g=24\text{\AA}$ with a correlation coefficient of 0.95. The data are extrapolated at high q from the constant asymptotic limit of the curve $q^4 I(q)$ and at low q from the Guinier plot. For a dilute system, the intensity can be then normalised in the usual way: $I_N(q)=I(q)/P$, with P total scattering power of the nanocrystals in the sample $P=(1/2\pi) \int_0^\infty q^2 I(q) dq$.

A Lognormal size distribution is used:

$$F(r) = (r \ln s / \sqrt{2\pi})^{-1} \exp \{-[\ln 2(\pi/\mu)/2 \ln s]\},$$

(μ is the algebraic mean of the distribution and s the geometric standard deviation).

For this distribution the n th moments of S are related to s and μ in a very simple way:

$$\langle S^n \rangle = \mu^n \exp \{k^2 \ln^2(s/2)\}.$$

Consequently, the linear size S_i are [10] :

$$S_i = \exp (\ln \mu + k_i \ln^2 s), \text{ with } k_i = 5/2, 7/2, 4, 9/2 \text{ and } 7 \text{ for } i=d, l, f, v \text{ and } g, \text{ respectively.}$$

For a given shape defined by the coefficients α_i , the linear sizes S_i are obtained from the characteristic parameters. When the values of $\text{Log}(S_i)$ are plotted versus k_i , if a straight line is obtained it indicates that a lognormal distribution conveniently approximate the real size distribution (figure 3). The geometric mean and the standard deviation for the lognormal distribution are obtained from the slope and the origin of the straight line. Moreover if the approximation made for the particle shape is consistent, the size obtained from the differential parameter is coherent with those obtained from the integral parameters.

Results and Discussion

The plot $q^4 I_N(q) = f(q)$ is given in figure 2. One finds $G(0)=0.020 \pm 0.003 \text{\AA}^{-1}$. This non-zero value shows that there are angularities at the surface of the particles. This value has been compared to the theoretical values of $G(0)$ obtained for different models of shape with similar radius of gyration $R_g=24\text{\AA}$. For a cylindrical shape with the height equal to the diameter $2A$, $G(0)=(8/3\pi)/(A+H)=0.015$. For polyedral shapes with low anisotropy (hexagonal shape with $H=2A$, cubic shape, parallelepipedon with $A=B=0.8C$ etc...) $G(0)$ is about 0.015 to 0.020. This allows to reveal the polyedric shape for the nanocrystals.

figure 2: Porod plot for the normalized scattered intensity.

figure 3 : Logarithmic plot of the size parameters S_i for a lognormal size distribution (spherical and cubic particles)

The characteristic parameters are obtained from the normalized intensity:

$$\langle l_p \rangle = 32.5 \pm 2 \text{\AA}, \langle l \rangle = 46 \pm 3 \text{\AA}, \langle f \rangle = 2430 \pm 120 \text{\AA}^2, \langle V \rangle = 136000 \pm 7000 \text{\AA}^3, \langle R_g \rangle = 23.5 \pm 1.5 \text{\AA}.$$

The values of r_i are calculated for the spherical shape and the cubic shape. The value of α_i are known for the spherical shape [8] $\alpha_f = \sqrt{(4\pi/5)}$; $\alpha_l = 3/2$; $\alpha_v = \sqrt[3]{(4\pi/3)}$; $\alpha_d = 3/4$; $\alpha_g = \sqrt{(5/3)}$ For a cubic shape: $\alpha_v = 1$; $\alpha_d = 2/3$; $\alpha_g = 2$; $\alpha_f = 0.941$; $\alpha_l = 0.887$. [9]

The plots $\text{Log}(S_i) = f(k_i)$ are given in the figure 3 for the two models of shape. For the spherical shape model the dots corresponding to the four integral parameters are well aligned but not the one corresponding to the differential parameter. This reveals agrees with the non zero value for $G(0)$. In the hypothesis of cubic shape the five dots are aligned. A linear regression taking into account the errors bars gives the parameters of the lognormal distribution describing the polydispersion of the system. This distribution is shown in figure 4. The experimental curve $I(q)$ has been compared to a simulation corresponding to the here above described distribution of cubic particles. The two curves are in satisfactory agreement (figure 5). The asymmetry of the distribution is low. The FWHM is $7\text{\AA}$ and the maximum value is close to $41\text{\AA}$.

figure 4: Lognormal size distribution deduced from the model of cubic particle shape.

figure 5: Measured scattered intensity and simulation obtained from the lognormal distribution of cubic particles.

Similar size distribution have been found by electron microscopy in close samples and agree with the distribution described by Lifshitz and Slezov [11] for a diffusion process governed by the coarsening of the particles.

Concluding remarks

The presence of angularities at the surfaces of nanoparticles of $\text{CdS}_x\text{Se}_{1-x}$ has been evidenced. Due to the limited accuracy of the measurement the shape of the nanocrystals cannot be precised. A model of cubic shape has been considered therefore more useful than a spherical shape to determine the size distribution function. As the nanocrystals crystallise in hexagonal structure the cubic shape does not correspond to a physical valid shape. Moreover this shape is not as isotropic that the one observed in electron microscopy images. Calculations have been made with that shape because it is the simplest polyedral shape. The size distribution defined in that case agree with that expected from the theory. The presence of angularities at the surface of the nanocrystals suggest that the domains near the surface evidenced in previous studies [1, 12] correspond to misoriented domains and not to amorphous zones. This hypothesis may be confirmed by a SAXS study of earliest stages of the growth of the nanocrystals. This study is in progress.

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