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Citation: [Review of Scientific Instruments](#) **66**, 1338 (1995); doi: 10.1063/1.1146472

View online: <http://dx.doi.org/10.1063/1.1146472>

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***In situ* synchrotron radiation small-angle x-ray scattering study of the kinetics of growth of CdTe nanocrystals in borosilicate glass**

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(Presented on 18 July 1994)

A number of isolator–semiconductor nanocrystal composites exhibit quantum confinement effects and nonlinear optical properties. In this work, the formation and growth of CdTe and CdTe_{0.9}S_{0.1} nanocrystals immersed in a borosilicate glass host matrix were studied by small-angle x-ray scattering using synchrotron radiation during *in situ* annealing in the 560–580 °C temperature range. The values of the average radii of the CdTe nanocrystals determined by using Guinier plots for different annealing times (20–30 Å) agree with those obtained from optical absorption spectroscopy measurements. The nanocrystal size distribution depends on the thermal history and composition of the samples. The existence of other structural heterogeneities having an average size of several hundred ångstroms was detected. © 1995 American Institute of Physics.

I. INTRODUCTION

Nonlinear optical properties have been observed in a number of glass–semiconductor nanocrystal composites. Most of the investigations reported in the literature mainly concern composites of borosilicate glass host matrices containing small CdS, CdSe, or CdSe_{1-x}S_x crystals.^{1,2} There is currently an increasing interest in new materials based on borosilicate glass containing CdTe_{1-x}S_x nanocrystals.^{3,4} Since the electronic Bohr radius a associated with CdTe crystals is larger than that of CdSe semiconductors ($a = 74$ Å for CdTe instead of 55 Å for CdSe), quantum confinement effects would more easily occur in CdTe-based composites than in those containing CdSe nanocrystals. The quantum electronic confinement is responsible for the nonlinear optical properties exhibited by these materials.

In order to establish the formation and determine the kinetics of growth of CdTe_{1-x}S_x nanocrystals immersed in borosilicate glass, an *in situ* small-angle x-ray scattering (SAXS) study during isothermal annealing was performed.⁵ The relevant structural parameters which were determined from the SAXS experiments are the average size and dispersion in size of nanocrystals. This study indicated the existence of a rather wide dispersion in size of the nanocrystals and proposed the use of a thermal pretreatment of the material to promote the narrowing in size distribution. On the other hand, the SAXS intensity produced by binary CdTe and quasibinary CdTe(S)-based composites was very weak, making the study of the kinetic of nanocrystal growth difficult.

This paper is a structural characterization of binary CdTe and quasibinary CdTe_{0.9}S_{0.1} nanocrystals immersed in a borosilicate glass matrix during *in situ* isothermal annealing using the SAXS technique with synchrotron radiation and optical absorption measurements.

II. SAMPLE PREPARATION AND HEAT TREATMENT

Batches of about 40 g of glass were prepared by mixing reagent-grade silica powder, sodium carbonate, boric acid, and zinc oxide (from Riedel). Additions of CdO, Te, and S (from Merck) were used as dopants. The mixture was melted in a high-purity alumina crucible placed in an rf induction coil furnace under a reducing atmosphere at 1400 °C for 50 min and then poured onto a cold, stainless steel plate. The glass was rapidly cooled in order to prevent or reduce the formation and growth of nanocrystals during cooling.⁶ The samples for optical absorption measurements received a pretreatment of 50 min at 450 °C and several isothermal treatments at 580 °C for different time intervals. The samples in which the formation of binary CdTe and quasibinary CdTe(S) nanocrystals occurs received pretreatments at temperatures of about 430 °C and further *in situ* treatments during SAXS measurements. For the final annealings at a constant temperature (560–580 °C), a specially designed high-temperature chamber⁷ was placed in the SAXS setup.

III. EXPERIMENTAL TECHNIQUES

The SAXS technique provides information on the structure of electronic heterogeneities with sizes ranging from about 5 up to 500 Å. The analysis of experimental data is particularly simple when the structure can be represented by a two-electronic density model composed of a dilute system of isolated “particles” immersed in a homogeneous matrix.

This model actually applies to systems composed of semiconductor nanocrystals immersed in a homogeneous glass matrix. In the samples of the present study, CdTe or CdTeS nanocrystals, having a characteristic diameter ranging from 10 to 100 Å, are embedded in a homogeneous solid

solution of borosilicate glass. The normal concentration of Cd and Te being rather low, the assumption about the dilute nature of the system is obeyed.

We studied one sample containing a nominal atomic ratio (Te/Cd)=1 and a second sample containing a minor amount of S, CdTe_{0.9}S_{0.1}. The samples received a pretreatment at a temperature of about 430 °C and were studied during isothermal annealing in the 560–580 °C temperature range.

The SAXS intensity was experimentally determined as a function of the modulus of the scattering vector q , which is related to half of the scattering angle θ and to the x-ray wavelength λ by $q=4\pi(\sin \theta)/\lambda$. The average size of the scatterer particles are deduced from the SAXS intensity $I(q)$ by using Guinier's law:⁸

$$I(q)=I(0)e^{-(1/3)R_g^2q^2}, \quad (1)$$

R_g being an average radius of gyration of the particles. Equation (1) applies to dilute systems of particles immersed in a homogeneous matrix. In the case of spherical nanocrystals $R_g=(3/5)^{1/2}R$, R being the nanocrystal radius. Since Guinier averaging gives much more weight to the larger particles, Eq. (1) yields useful structural information when the size distribution is narrow. A necessary condition for a direct application of Eq. (1) is its validity within a wide q range.

For a two-electronic density system, the extrapolated intensity $I(0)$ is related to structural parameters by

$$I(0)=(\rho_1-\rho_2)^2N\langle v^2 \rangle, \quad (2)$$

where ρ_1 and ρ_2 are the electronic densities of the phases, N the number of scatterers, and $\langle v^2 \rangle$ an average value of the scatterer volume. For systems composed of spherical particles with a narrow size distribution and constant electronic densities in the particles and matrix, we have

$$I(0)\propto NR^6 \quad \therefore N\propto I(0)/R^6 \quad \text{and} \quad V\propto I(0)/R^3. \quad (3)$$

Absorption optical spectra corresponding to the composites under study exhibit the so-called blue shift related to the presence of extremely small semiconductor crystals. Under the assumptions of the classic Efros and Efros model,² the photon energy E_R corresponding to the relative maximum in absorption in the optical spectrum is related to the energy gap E_g of the macroscopic crystal and to the average radius of R of nanocrystals (assumed spherical) by

$$E_R=E_g+\frac{\hbar^2\pi^2}{2R^2\left(\frac{1}{m_e}+\frac{1}{m_h}\right)}-\frac{1.8e^2}{\epsilon R}, \quad (4)$$

m_e and m_h being the effective mass of electrons and holes, respectively, and ϵ the dielectric constant of the material. Equation (4) permits the determination of the average size of the nanocrystals, provided that their size distribution is narrow. The existence of a wide size distribution reflects on the width of the characteristic relative maxima in absorption spectra.

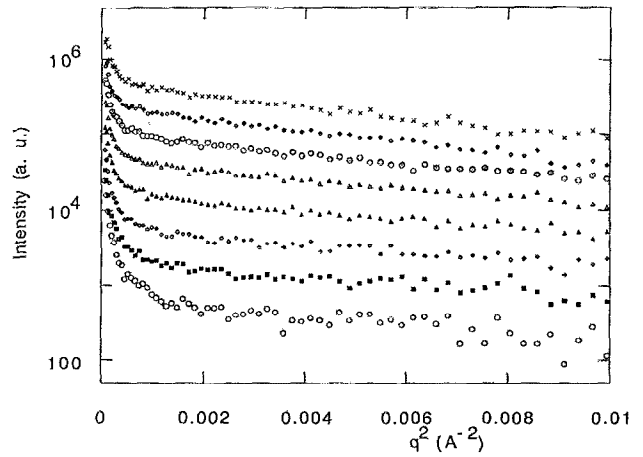


FIG. 1. SAXS intensity from borosilicate glass containing CdTe nanocrystals. Samples pretreated 13 h at 433 °C and annealed for 580 °C for different times: 2, 8, 15, 26, 36, 46, 55, and 63 min, from bottom to top. The curves were displaced vertically for clarity.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

SAXS experiments were performed at the synchrotron radiation laboratory LURE, Orsay, France, using the D24 workstation. This setup is equipped with an asymmetric, bent-germanium single crystal to monochromatize and focus the incident beam. An x-ray wavelength of 1.60 Å was selected and a pinholelike collimation was utilized for the incident beam. A position-sensitive detector was used to record SAXS spectra.

The plots of SAXS intensity in Fig. 1 correspond to a borosilicate glass in which Cd and Te were added to the batch in a proportion of 1:1. The studied sample was pretreated during 13.5 h at 433 °C and maintained at 580 °C during the measurements. The linear behavior in the $\log I$ versus q^2 plots within a large q range ($0.001 < q^2 < 0.01 \text{ \AA}^{-2}$) indicates the validity of the Guinier law [Eq. (1)] for the glass–CdTe nanocrystal composite.

Guinier plots corresponding to a sample composition CdTe_{0.9}S_{0.1} pretreated during 20 h at 430 °C and annealed at 580 °C also showed a clear linear behavior within a wide q range, as can be seen in Fig. 2, suggesting a narrow crystal size distribution. Nevertheless, other plots corresponding to a quasibinary sample with the same nominal composition (CdTe_{0.9}S_{0.1}) but with a longer pretreatment of 62 h at 430 °C did not exhibit any linear range, indicating, in this case, the existence of a wide crystal size distribution.

The slope of the straight portion in Guinier plots is associated with the average radius of gyration of the nanocrystals [Eq. (1)]. The slope and consequently the radius increase monotonically with the annealing time, as can be seen in Fig. 1 for the sample containing CdTe nanocrystals. A similar behavior was exhibited by the SAXS curves, corresponding to CdTe_{0.9}S_{0.1} samples, plotted in Fig. 2.

A sharp decrease in SAXS intensity for increasing q at very small angles is apparent for both composites (containing CdTe and CdTe_{0.9}S_{0.1} nanocrystals), even in data corresponding to samples which were submitted to very short an-

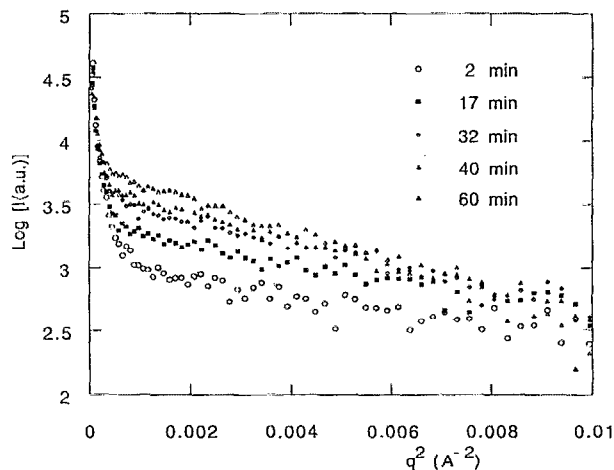


FIG. 2. SAXS intensity from borosilicate glass containing $\text{CdTe}_{0.9}\text{S}_{0.1}$ nanocrystals pretreated during 20 h at 430°C and annealed at 580°C during the times indicated.

nealing. We associate this contribution to the SAXS intensity with the existence of coarse heterogeneities in electronic density, formed during the cooling of the samples. These heterogeneities may be produced by some type of noncontrolled segregation of Cd and/or Te, or CdTe(S) crystals. This indicates that the microstructure of samples containing CdTe(S) is composed of heterogeneities with a bimodal size distribution, the small ones being CdTe (or $\text{CdTe}_{0.9}\text{S}_{0.1}$) nanocrystals whose characteristic size increases with time and large, poorly defined aggregates having an approximately time-constant size of about 200 \AA .

Optical absorption spectra with CdTe samples, pretreated 50 min at 450°C and annealed *ex situ* at 580°C , exhibit the characteristic blue shift of the absorption edge, as can be seen in Fig. 3. This confirms the existence of small CdTe crystals immersed in the borosilicate glass matrix, detected by SAXS. The relative maxima in absorption, which are apparent in Fig. 3, are associated with the presence of nanocrystals having a narrow size distribution in the range below 100 \AA . From the observed maxima and using Eq. (4), the average radii of nanocrystals were determined.

The time variation in the average radii of the nanocrystals, determined using Guinier law and assuming a spherical shape, is represented in Fig. 4 for samples containing CdTe and $\text{CdTe}_{0.9}\text{S}_{0.1}$. In the same figure, the average radii corresponding to samples containing CdTe, determined from optical absorption measurements, are also plotted. We can see that the average radius obtained from SAXS results for CdTe crystals is always slightly larger than that determined from the absorption experiments using Eq. (4). This difference is expected because the average in the radius determined using Guinier law gives much more weight to large nanocrystals. Due to the weak SAXS intensity produced by samples containing CdTe and $\text{CdTe}_{0.9}\text{S}_{0.1}$ nanocrystals, we were unable in the present work to determine the size distribution function using classical procedures as in a precedent investigation concerning samples with high sulfur contents.⁵

The radii of CdTe and $\text{CdTe}_{0.9}\text{S}_{0.1}$ nanocrystals increase

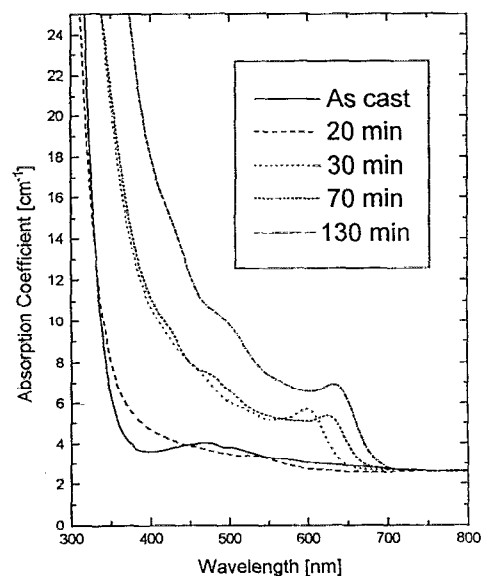


FIG. 3. Optical absorption coefficient of a composite containing CdTe nanocrystals. The sample was pretreated 50 min at 450°C and annealed at 580°C for the times indicated.

linearly with time during the first hour of annealing at 580°C . This time dependence, not being that expected from the basic and simple models for diffusion-controlled growth, suggests that a complex process involving more than one competing mechanism occurs.

Assuming a narrow size distribution and a spherical shape for nanocrystals, Eqs. (3) were applied to estimate the variation with time of the number, N_n , and the total volume fraction, V_n , of CdTe and $\text{CdTe}_{0.9}\text{S}_{0.1}$ nanocrystals. $I(0)$ was determined by extrapolating the linear part of Guinier plots (Figs. 1 and 2). N_n and V_n are plotted in Fig. 5. The number of nanocrystals increases during the first 20 min and decreases for longer annealing times. The volume fraction occupied by nanocrystals increases up to saturation after 30 min. The behaviors of $V_n(t)$ and $N_n(t)$ indicate that, during the first stages of the process, nanocrystals grow and, simul-

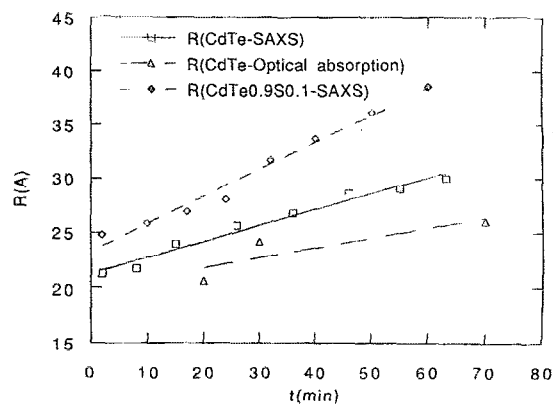


FIG. 4. Time evolution of the radius of CdTe and $\text{CdTe}_{0.9}\text{S}_{0.1}$ nanocrystals determined from Guinier plots. The values of the radii of CdTe nanocrystals obtained from optical absorption spectra are also plotted.

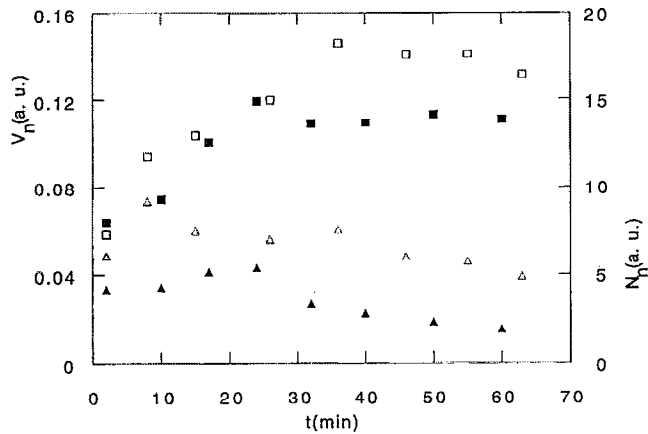


FIG. 5. Time variation of the number of nanocrystals N_n (Δ) and their total volume fraction V_n (\square) corresponding to samples containing CdTe (empty symbols) and CdTe_{0.9}S_{0.1} (filled symbols) nanocrystals.

taneously, additional crystals nucleate. At advanced stages (after 30 min), the total crystal volume fraction remains constant and the nanocrystal number decreases. This decrease in number of nanocrystals is expected when crystal growth occurs by coarsening (the larger crystals growing at the expense of the smaller ones).

V. CONCLUSION

This SAXS study demonstrated the existence, determined the size, and characterized the kinetic of growth of CdTe and CdTe_{0.9}S_{0.1} nanocrystals immersed in borosilicate glass. The characterization by optical absorption measurements was in good agreement with SAXS results. The thermal history of the samples strongly affects the nanocrystal size distribution.

The presence of additional coarse heterogeneities was detected. In order to obtain additional information on the composition of nanocrystals and establish the nature of the coarse heterogeneities, further investigation using the anomalous small-angle x-ray scattering technique near the Cd and Te absorption edges is planned.

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