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XAFS Study of $\text{CdTe}_{1-x}\text{S}_x$ Semiconductor Glass Composites

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Abstract. We have measured the X-ray absorption spectra of $\text{CdTe}_{1-x}\text{S}_x$ nanocrystals grown in a borosilicate matrix, for $x = 0, 0.1, 0.4$ and 0.7 . The appearance and the growth of the nanocrystals in isothermal heat-treatment at 580°C , observed in optical measurements, were correlated to the evolution of the XANES at the cadmium edge corresponding to the progressive substitution of oxygen atoms by chalcogens atoms. The final mean environment of the cadmium atoms in nanocrystals seems to be closer to CdS than to CdTe, for any value of x . On the other hand significant deviations from CdO pure environment were observed in non-treated samples, correlated to the increase in the sulfur content in the initial glass. These features were ascribed to the existence of early CdS clusters.

1. INTRODUCTION

The quantum confinement strongly modifies the optical properties as absorption, photoluminescence and the non linear refractive index and opens up interesting problems in the physics and chemistry of low dimensional systems. Furthermore, the nonlinear properties of these materials may have important applications in optoelectronics, such as picosecond optically bistable switches and fibers or other wave guides of highly nonlinear materials. Quantum confinement effects occur when the microcrystallite sizes are comparable to the Bohr radii. For II-VI semiconductors, these radii are typically in the range $20 \text{ \AA}$ to $80 \text{ \AA}$. Most experimental observations have been concentrated in $\text{CdSe}_{1-x}\text{S}_x$ doped glasses. Recent studies of dynamics of optical nonlinearities for CdTe using the pump and probe technique show femtosecond response times in the absorption range [1]. These results suggest new possibilities for all-optical photonic switching devices using $\text{CdTe}_{1-x}\text{S}_x$ -doped glasses as tunable nanosystems in the red and near infrared range.

2. EXPERIMENTAL

The glass system used in this study is $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-ZnO} + 3\%$ in weight of doping elements Cd, Te and S. Different ratio of Te and S were introduced to get $\text{CdTe}_{1-x}\text{S}_x$ with $x = 0, 0.1, 0.4$ and 0.7 , and a molar ratio Te+S/Cd always close to 1. The initial glasses are prepared by quenching a melt of initial components from 1400°C to room temperature, followed by a preliminary annealing at 430°C for removing strain. Subsequent isothermal treatments at 580°C were carried out to achieve the nanocrystallites. Optical absorption and photoluminescence measurements showed quantum confinement (confinement energies from 0.8 to 1.6eV) [2]. The nanocrystals average radius was measured by TEM and optical absorption at each stage of the treatment [3].

The XAS spectra were measured at the Cd K edge (26711eV), in the transmission mode, at the D41 XAS workstation of the DCI storage ring (LURE, Orsay). The data were acquired at room temperature using a Si (331) channel-cut monochromator. Owing to dilution and small size of the samples, a low signal over noise ratio was obtained and a complete EXAFS analysis was not possible for these samples. Only XANES data are presented here.

3. RESULTS

XANES spectra of the glass corresponding to $x = 0.1$ at different stages of the heat treatment are shown in figure 1. The reference compounds are given for comparison: CdS and CdTe bulk and a cadmium doped reference glass. In the reference glass the cadmium atoms are perfectly incorporated in the matrix with four oxygen atoms as first neighbors [4].

The features present in the spectra are broad due to the large core hole level at the cadmium K edge ($\approx 7\text{eV}$), only the amplitude and position of the two smooth structures in the first 50eV above the edge can be discussed. The intensity of these features decrease with the thermal treatment. The XANES data of non-treated sample are identical to the one of the reference glass, corresponding to the full incorporation of cadmium atoms in the oxygen atom environment. The maxima of these structures are smoother in the treated samples, for 15 and 25 minutes possible variations between the different stages of treatment are within the experimental uncertainty. The main variation in the cadmium environment occurs in the first 25

minutes of treatment corresponding to the substitution of oxygen nearest neighbors by chalcogen atoms. The molar ratio Te+S/Cd is close to 1, then the cadmium atoms are assumed to be fully incorporated in the semiconductor structure in the last stages of treatment. For $x = 0.1$ the optical absorption spectra are those of the expected $\text{CdTe}_{0.9}\text{S}_{0.1}$ nanocrystals [3].

Figure 1- XANES spectra for $\text{CdTe}_{0.9}\text{S}_{0.1}$ doped glass at Cd K edge. Reference glass (a), non treated glass (b), sample treated at 580°C during 15 min (c), 25 min. (d), 60 min. (e), CdTe ref. (f), CdS ref. (g).

Figure 2- XANES spectra at Cd K edge for non treated samples with different sulfur contents. CdS reference (a), $\text{CdTe}_{0.3}\text{S}_{0.7}$ (b), $\text{CdTe}_{0.6}\text{S}_{0.4}$ (c), $\text{CdTe}_{0.9}\text{S}_{0.1}$ (d), CdTe (e) and reference glass (f).

A great similarity between the XANES of the treated samples and CdTe bulk should be observed however the XANES spectra are much closer to the one of CdS bulk (figure 1). In order to clarify these results we performed XANES simulations on CdTe and CdS using FEFF6 code [5]. CdS bulk crystallizes in the wurtzite structure whereas CdTe bulk crystallizes in the zinc blend structure. The simulations showed that blend and wurtzite structures are undistinguishable at Cd K edge. The differences observed in experimental CdS and CdTe spectra (fig. 1 curves f and g) are more likely due to electronic effects of scattering atoms.

Figure 2 shows the XANES spectra of non-treated glasses with different ratios S/Te ($x = 0, 0.1, 0.4$ and 0.7). For $x = 0$ and 0.1 the XANES features are close to the reference glass. For higher sulfur content we observe significant deviations from CdO pure environment. This suggest the existence of early CdS clusters, as already observed in other CdS-doped glasses [6]. Earliest CdS clusters can also be in part responsible for the CdS-like features in the XANES of treated samples. Further investigations are needed to elucidate this point. In order to get a better energy resolution and signal to noise ratio new measurements will be made at the cadmium L_{III} edge in fluorescence mode.

4. CONCLUDING REMARKS

In this study we have measured the X-ray absorption spectra of $\text{CdTe}_{1-x}\text{S}_x$ nanocrystals at Cd K edge. We have followed the progressive substitution of oxygen by chalcogen atoms during the thermal treatment of Cd(Te,S) doped glasses. At high sulfur content in as cast samples the XANES features are no more those of a full oxygen atoms environment probably due to the presence of early CdS clusters.

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