Thermal, structural and optical properties of \{CdS\}–Na\textsubscript{86}X composites

Gerardo Gutierrez-Juarez, Orlando Zelaya-Angel, Juan J. Alvarado-Gil, Heliose de O. Pastore, Jos\'{e} S. Barone, Manuel Hernandez-Velez and Leticia Baios

\textit{Departamento de Fisica, CINVESTAV-IPN, A. P. 14-740 Mexico D. F. 07000, Mexico}
\textit{Instituto de Quimica, Universidad Estadual de Campinas, CP 6154, CEP 13083-970, Campinas, S. P., Brazil}
\textit{Instituto Superior Pedagogico E. J. Varona, La Habana, Cuba}
\textit{IIM-UNAM, C. P. 703, Mexico D. F. 04511, Mexico}

Thermal, structural and optical properties of CdS superclusters grown in zeolite Na\textsubscript{86}X are reported. The interest in this work arose in the need to study CdS prepared in the zeolite host, at high concentrations (>19%), in order to observe porosyte behaviour and CdS aggregate properties. The semiconductor–zeolite composite was studied using X-ray diffraction analysis and photoacoustic technique (PAS). The properties of semiconductor CdS embedded in a zeolite matrix were analysed as a function of the CdS concentration by monitoring Cd concentration (atom%) by chemical analysis. The results show that as the concentration of CdS increases, the thermal diffusivity, capacity, conductivity and the band-gap increase up to a point where the zeolite lattice collapses. From this point on, all these thermal properties diminish and the band-gap is the same as for bulk CdS.

Experimental

Sample preparation

The zeolite used in these work was a commercial synthetic material from Laporte with a silicon: aluminum ratio of 1.23:1 and of formula Na\textsubscript{86}Al\textsubscript{6}Si\textsubscript{13}O\textsubscript{46} \cdot 250H\textsubscript{2}O. The relative concentration of CdS inside the zeolite host ranged from the supercluster limit\textsuperscript{4} to a mixture of the zeolite with the semiconductor. \{CdS\}–Na\textsubscript{86}X powder composites were prepared by chemical synthesis and their crystalline structure was established by X-ray diffraction analysis.

Syntheses of samples of \{CdS\}–Na\textsubscript{86}X were carried out as follows: 2\textsubscript{n} g of zeolite powder were added to 0.1 mol dm\textsuperscript{-3} ammonium nitrate solution and stirred well at 363 K, for 5 h, in order to effect ion exchange. Then the solution was filtered and extensively washed with deionized water. The solid obtained was mixed with water and to this suspension, 2\textsubscript{n} g of thiourea and \( \eta \) g of cadmium chloride were added and vigorously stirred during 2 h, at 363 K. The solid was then filtered, thoroughly washed with deionized water and air-dried. The CdS concentration in the composite is a function of the parameter \( \eta \).

X-Ray analysis

The crystalline structure of the samples was established by X-ray diffraction using a Siemens D-500 diffractometer monitored at 35 kV and 15 mA, with Cu-K\textsubscript{x} radiation (\( \lambda = 0.15406 \) nm) at a scan speed of 1 degrees min\textsuperscript{-1} (in 2\textdegree) with Diffrac-AT software [version 3.2, SOCABIM (1993)] with a sample surface area of 6.45 cm\textsuperscript{2}; JCPDS PDF 41-1049 for CdS was used to reference the peaks.

PA technique

The PA effect looks directly at heat generated in a sample due to non-radiative deexcitation processes following the absorp-
tion of light. In a conventional experimental arrangement, a sample is enclosed in an air-tight cell and exposed to a chopped light beam. As a result of the periodic heating of the sample, the pressure in the cell oscillates at the chopping frequency and can be detected by a sensitive microphone coupled to the cell. The resulting signal depends not only on the amount of heat generated in the sample (and, hence, on the optical absorption coefficient and the light-into-heat conversion efficiency of the sample) but also on how the heat diffuses through the sample, as determined by the thermal diffusivity.

Optical spectra

The photoacoustic absorption spectra were obtained in the region 350–750 nm by the use of a standard photoacoustic spectrometer. The experimental set-up used consists of a 1000 W xenon lamp (Oriel), a variable-frequency chopper set at 17 Hz, a monochromator, an air-filled aluminium cell with a condenser microphone, a low-noise preamplifier, and a lock-in amplifier. The sample compartment, in which the powdered \( \text{CdS}-\text{Na}_2\text{X} \) composite was placed, is a cylindrical chamber. The photoacoustic signal is preamplified before providing the input to the signal channel lock-in amplifier (SR-850). The resultant photoacoustic spectra are recorded in a computer, which simultaneously displays the wavelength-dependent signal intensity.

Thermal diffusivity, \( \alpha \)

The thermal diffusivity, \( \alpha \), is the quantity that measures the rate of diffusion of heat in a material. Apart from its own intrinsic importance, its determination provides the value of the thermal conductivity, \( k \), if the density, \( \rho \), and the heat capacity at constant pressure, \( C_p \), are known (\( \alpha = k/\rho C_p \)). Physically, the inverse of \( \alpha \) is a measure of the time required to achieve thermal equilibrium in a given material.

In order to perform the photoacoustic measurements for thermal diffusivity, circular pieces of the composite powder (300 µm thick, 3 mm radius) were prepared by pressing the powder at a pressure of 5.1 \( \times 10^3 \) atm.

The experimental arrangement for the PA measurements of the thermal diffusivity is shown schematically in Fig. 1. It consists of an Oriel 250W halogen lamp the polychromatic beam of which is mechanically chopped and focused onto the sample. The sample is mounted in such a way as to cover the sample surfaces. A thermocouple was attached on the opposite surface using thermal paste. In this way, the temperature rise method, under continuous white-light illumination

![Fig. 1 Schematic arrangement for the PA measurements of thermal diffusivity](image)

Heat capacity, \( \rho C_p \)

The heat capacity per unit volume, \( \rho C_p \), was measured using the temperature rise method, under continuous white-light illumination. The experimental arrangement is shown in Fig. 2. The samples were sprayed on both surfaces with a very thin film of black paint. A light-absorbing surface and the same heat-transfer coefficient were thus assured for each side of the sample. The samples were adiabatically suspended in a Dewar flask which was subsequently vacuum sealed. Under these conditions, the main heat-loss mechanism was by radiation. The Dewar had an entrance glass window through which the continuous white-light beam was focused onto one of the sample surfaces. A thermocouple was attached on the opposite surface using thermal paste. In this way, the temperature evolution of the back surface could be monitored as a function of the time. Care has been taken to prevent the heating light from reaching the thermocouple. Since the samples thicknesses are typically in the order of 300 µm and much smaller than their widths (e.g. 0.6 cm), the simple one-dimensional heat diffusion equation with radiation losses could be applied to our measurements. Solving the one-dimensional heat diffusion equation, it can be shown that the long-term time evolution (i.e., for times greater than the heat diffusion time, approximately \( H^2/\alpha \), where \( H \) is the sample thickness and \( \alpha \) the thermal diffusivity) of the back surface temperature rise is given by:

\[
\Delta T = (I_o \alpha t/k)\left[1 - \exp(-t/\tau)\right] \quad (1)
\]

where \( I_o \) is the intensity of the incident light beam and \( \tau = I_o C_p/2H \) is the rise time. Here, \( H = 4\sigma T_0^4 \) where \( \sigma \) is the Stefan–Boltzmann constant, \( T_0 \) is the ambient temperature, and \( H \) is the radiation heat transfer coefficient. \( \tau \) is determined by fitting the experimental result with eqn. (1). The thermal conductivity \( k \) is readily obtained from the previously value of \( \alpha \) calculated by using \( k = \alpha \rho C_p \).

Results and Discussion

Chemical and X-ray diffraction analysis

The parameter \( \eta \) was fixed to values of 0.05, 0.10, 0.20, 0.50 and 0.80. Fig. 3(a) and (b) illustrate the plot of number of Cd
ions per unit cell and wt.% CdS, measured by chemical analysis, as a function of $\eta$. Table 1 lists the different obtained Cd percentages for each $\eta$. From these data, it can be observed that the concentration of CdS for the first sample is at the limit of the unit-cell capacity of ion exchange, taking into account all its cationic sites. In the other samples, the CdS concentration is well over this limit, leading to the conclusion that CdS crystallites are forming into and around the zeolite crystals and at these CdS concentrations superclusters are formed.

Superclusters are viewed as three-dimensional arrays of mutually interacting clusters (quantum dots) with their geometric structure imposed by the zeolite internal pore structure. From IR spectroscopy measurements, it has been found that CdS superclusters have to be strongly coupled to the zeolite lattice. This strong coupling arises from the interactions among clusters through the zeolite framework. In our samples, all measurements were performed after the CdS cluster interaction has overcome the critical threshold at which, statistically, these clusters must now populate adjacent cluster positions, giving origin to the superclusters. The critical threshold appears at $4 \pm 1$ wt.% inside the sodalite cages of the Y zeolite,\(^3\) the cages in X and Y zeolites are about the same size.\(^6\) An observed abrupt transition in optical absorption measurements suggests that the cluster aggregation process may be a three-dimensional percolation process.\(^2\) Based on the this consideration, it is expected in our case that increasing the CdS concentration leads to the entire zeolite structure suffering an increasing internal pressure. This effect is due to the growth of population in neighbouring cluster positions and their interactions throughout the zeolite lattice. If the interactions among clusters continues to grow, there will be a point where the zeolite framework cannot withstand the internal pressure and result in crumbling. This was confirmed by powder X-ray diffraction.

Fig. 4 shows the X-ray profiles of samples from 16.96 to 40.56 wt.%. The pattern of pure Na,S,X and hexagonal CdS are included for comparison. Fig. 4(a) shows the zeolite diffraction diagram, the crystalline lattice of which has cubic symmetry. Fig. 4(b)–(e) display the patterns of composites with increasing CdS concentration. It can be observed that even at only 16.96 wt.% CdS, peaks belonging to the semiconductor crystalline phase are superimposed with peaks corresponding to the CdS phase. Upon increasing the CdS concentration, X-ray analysis shows that peaks corresponding to the zeolite phase become less intense, and those identified with CdS are better defined. In Fig. 4(e), only the CdS contribution appears in the range of 2θ where the zeolite usually presents a crystalline pattern and no clear features are observed for the zeolite. Therefore, we conclude that the zeolite becomes amorphous. The same behaviour was observed for the sample with 51.51 wt.% Cd.

As expected, the evaluation of the zeolite lattice parameter $a$ is encumbered by the significant presence of CdS clusters. Table 1 lists values of $a$, together with the standard deviations; all the values are the same within statistical deviation.

**Table 1** The $\eta$ parameter, percentage of Cd, lattice parameter and $E_\text{g}$ values for \{CdS\}-Na,S,X zeolites

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>Cd (%)</th>
<th>$a_0$/Å</th>
<th>$E_\text{g}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>16.96</td>
<td>24.9 ± 0.1</td>
<td>2.36 ± 0.03</td>
</tr>
<tr>
<td>0.10</td>
<td>21.40</td>
<td>24.8 ± 0.1</td>
<td>2.43 ± 0.03</td>
</tr>
<tr>
<td>0.20</td>
<td>31.40</td>
<td>25.0 ± 0.3</td>
<td>2.46 ± 0.03</td>
</tr>
<tr>
<td>0.50</td>
<td>40.56</td>
<td>amorphous</td>
<td>2.34 ± 0.03</td>
</tr>
<tr>
<td>0.80</td>
<td>51.51</td>
<td>amorphous</td>
<td>2.34 ± 0.03</td>
</tr>
</tbody>
</table>

The photoacoustic absorption spectra of four samples are shown in Fig. 5. For the band-gap energy value ($E_\text{g}$) determination we chose the ‘knee’ criterion.\(^2\) Theoretical models for a more exact calculation of $E_\text{g}$ from photoacoustic data are reported in the literature.\(^28\) However, we are only interested in the general trends of $E_\text{g}$ in the composites studied. The use of the ‘knee’ method is illustrated in the insert of Fig. 5 and $E_\text{g}$ values for the samples are listed in Table 1. Fig. 6 illustrates the $E_\text{g}$ values as a function of the wt.% CdS. The Na,S,X zeolite is an insulator, thus its $E_\text{g}$ value is expected to be larger than 3.54 eV, the limit of detection of our experimental set-up. The $E_\text{g}$ value for pure powdered CdS was measured by this technique and found to be 2.36 ± 0.03 eV. $E_\text{g}$ values for 16.96, 40.56 and 51.51 wt.% \{CdS\}-Na,S,X composites are nearly the same as for pure CdS.\(^2\) That means that at these concentrations there are no quantum size effects. However, at 21.40 and 31.40 wt.%, just prior to the total collapse of the zeolite structure, $E_\text{g}$ is higher than that of pure CdS indicating that at...
Fig. 4 X-Ray diffractograms. (a) Pure zeolite, (b)-(e) Samples with 10.96, 21.40, 31.40 and 40.56 wt.% CdS respectively, in these four diffractograms the solid lines are the peaks of the CdS phase and the dashed lines arise from the crystalline structure of the zeolite; (f) pure hexagonal CdS.

Fig. 5 Photoacoustic absorption spectra for $\eta = 0.05, 0.10, 0.20$ and 0.50

these concentrations, although the clusters are not small, there is a quantum size-type influence on $E_a$ values. This dependence can be explained by considering that at these concentrations, the CdS clusters in the zeolite are under pressure and are strongly interacting with each other. Therefore, it is expected that the CdS clusters experiment a shrinkage. An immediate consequence of this is to obtain $E_a$ values. After amorphitization of the zeolite, for the 40.56 and 51.51 wt.% composites, the composites are a mixture of silicoaluminate with crystalline aggregates of CdS and $E_a$ values measured for these mixtures, obviously, must be closer to that corresponding to crystalline CdS. For CdS concentrations in the range 16.96–31.40, we are confident that the CdS has not lost its chemical identity inside the cages. In other words, the formation of a new chemical compound from zeolite and CdS can be ruled out, since X-ray analysis does not show any pattern corresponding to a different crystalline substance. The same analysis is valid for CdS concentrations higher than 31.40
wt.%. Hence it can be concluded that we are essentially measuring $E_s$ for the CdS encapsulated in Na$_{x}$X zeolite up to a limiting content of 31.40%.

**Measurement of thermal properties**

In the thermal diffusivity ($\alpha$) measurements using the OPC detector, the pressure fluctuation $\delta p$ in the air chamber, for the rear-side illumination configuration, Fig. 1, is predicted by the thermal diffusion model and given by

$$\delta p \approx \frac{\gamma P_g (T_a) \alpha_s}{2 \pi n T_0 k_s f} \left\{ \exp \left[ j (\omega t - \pi/4) \right] / \sin \left[ \omega t / (\alpha_i) \right] \right\}$$

where $\gamma$ is the air heat capacity ratio, $P_g (T_a)$ is the ambient pressure (temperature), $I_0$ is the radiation intensity, $f$ is the modulation frequency and $\alpha_i$ is the length, thermal conductivity and thermal diffusivity of medium $i$, respectively. Here, the subscript $i$ denotes the absorbing sample (s) and the air (g), respectively. $\alpha = (1 - j) \alpha_i$, $\alpha_i = (\pi f / \alpha_i)^{1/2}$ is the complex thermal diffusion coefficient of material $i$. In arriving at eqn. (2) we have assumed that the sample is optically opaque to the incident radiation and that the heat flux into the surrounding air is negligible. The optical opaqueness condition means that all the radiation is absorbed at the outer sample surface ($z = -l/2$ in Fig. 7). Eqn. (2) is further simplified in two limiting cases depending upon the thermal properties of the sample. For a thermally thin sample, namely $l_1, \alpha_s \ll 1$, it reduces to:

$$\delta p \approx \frac{\gamma P_g (T_a) \alpha_s}{2 \pi n T_0 k_s l_1} \left\{ \exp \left[ j (\omega t - 3\pi/4) \right] / f^{3/2} \right\}$$

i.e. the detected signal should decrease as $f^{3/2}$ as one increases the modulation frequency. If $l_1 \alpha_s \gg 1$, the samples are thermally thick, and one obtains:

$$\delta p \approx \frac{\gamma P_g (T_a) \alpha_s}{2 \pi n T_0 k_s l_1} \left\{ \exp \left[ j (\pi t - \pi/2) \right] / f \right\}$$

$$\times \exp \left[ j (\omega t - \pi/2 - l_1 \alpha_s) \right]$$

Eqn. (3) means that, for a thermally thick sample, the amplitude of the PA signal decreases exponentially with the modulation frequency as $(1/f) \exp (-a f^3/2)$, where $a = (\pi f / \alpha_i)^{1/2}$. From eqn. (3) and (4) the thermal diffusivity $\alpha_i$ can be obtained by fitting the data in the corresponding regime. However, in the thermally thick regime, small changes in the diffusivity give place to larger changes in the PA signal. In this regime $\alpha_i$ can be obtained by fitting the experimental data with the coefficient $b$, by using eqn. (4) in the form:

$$S = \left( A / f \right) \exp (-b f^{3/2})$$

The constant $A$, in the measured signal $S$, apart from geometric factors, includes all other factors such as the gas thermal properties, and so on. We thus have two adjustable parameters $A$ and $b$ to describe the PA monitoring of the thermal diffusivity of the sample. In Fig. 8, we show the PA signal amplitude as a function of the modulated square root of the frequency for 51.51 wt.% CdS sample. The solid curve in this Figure represents the fitting of the experimental data to eqn. (5). The resulting value of $\alpha$ from the data fitting was $(2.60 \pm 0.31) \times 10^{-3}$ cm$^2$ s$^{-1}$.

**Table 2**, Thermal parameters as functions of percentage of CdS

<table>
<thead>
<tr>
<th>CdS (wt.%)</th>
<th>$\alpha$ /10$^{-3}$ cm$^2$ s$^{-1}$</th>
<th>$\rho C_p$ /W cm$^{-3}$ K$^{-1}$</th>
<th>$k$ /10$^{-3}$ W cm$^{-1}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.40 $\pm$ 0.17</td>
<td>1.26 $\pm$ 0.15</td>
<td>1.76 $\pm$ 0.42</td>
</tr>
<tr>
<td>16.96</td>
<td>3.00 $\pm$ 0.14</td>
<td>1.16 $\pm$ 0.16</td>
<td>3.48 $\pm$ 0.84</td>
</tr>
<tr>
<td>21.40</td>
<td>2.60 $\pm$ 0.31</td>
<td>1.27 $\pm$ 0.15</td>
<td>3.30 $\pm$ 0.79</td>
</tr>
<tr>
<td>31.40</td>
<td>3.40 $\pm$ 0.41</td>
<td>2.68 $\pm$ 0.32</td>
<td>9.11 $\pm$ 2.20</td>
</tr>
<tr>
<td>40.56</td>
<td>2.10 $\pm$ 0.25</td>
<td>1.45 $\pm$ 0.17</td>
<td>3.05 $\pm$ 0.73</td>
</tr>
<tr>
<td>51.51</td>
<td>1.50 $\pm$ 0.18</td>
<td>1.80 $\pm$ 0.21</td>
<td>2.70 $\pm$ 0.65</td>
</tr>
</tbody>
</table>

the zeolite becomes less porous as CdS wt.% increases. The minimum crystallinity of the composite is conserved in that range. Under these conditions, it is expected that heat flowing is faster. Thus the diffusivity $\alpha$ increases as CdS wt.% increases as has been reported for ceramic materials.\(^{28}\) For CdS wt.% > 31.40, the zeolite becomes amorphous, and heat does not flow as easily as for the samples with CdS wt.% < 31.40. The loss of crystallinity in the composite is an impediment for effective heat transfer, despite the probable higher density. Fig. 9(a) clearly shows that $\alpha$ diminishes for CdS wt.% > 31.40.

Fig. 10 shows the back surface temperature rise as a function of time, after commencement of illumination, for a sample with wt.% CdS = 21.40. The solid line represents the result of the best fit of the experimental data to eqn. (1) using $\tau$ as an adjustable parameter. From the value of $\tau$ obtained in this way, one obtains the experimental value of the heat capacity from $\rho C_p$, for the sample with 21.40 wt.% CdS. The same procedure was followed in order to obtain the $\rho C_p$ values for all the sample. $\rho C_p$ values are given in Table 2 and $\rho C_p$ vs. wt.% CdS is plotted in Fig. 9(b). It is known that both crystalline and amorphous phases of the same compound have nearly equal heat capacities.\(^{39}\) However, in the vicinity of a phase transition, the behaviour is different. As can be observed in Fig. 9(b), the heat capacity of wt.% 31.40 sample abruptly separates from the remainder of the $\rho C_p$ value. We know that this concentration is at a critical limit for the zeolite integrity, above which the crystalline-to-amorphous phase transition occurs. This is consistent with the well known behaviour of heat capacity at critical points. This is an obvious example of detection of a phase transition from measurements of heat capacity per unit volume.

Fig. 9(c) shows the thermal conductivity $k$ as a function of percentage CdS and Table 2 lists the $k$ values for all the CdS percentages used. It is evident from Fig. 9(c) and Table 2 that $k$ reaches a maximum at 31.40 wt.% CdS. The analysis of this phenomenon is essentially the same as for the values of $\alpha$. Heat flows faster through a less porous crystalline material than in a more porous or amorphous material. Hence, a larger amount of heat flows per unit time for the 31.40 wt.% CdS composite.

**Conclusion**

In summary, we have investigated the CdS superclusters encapsulated in Na\textsubscript{12}X matrices, from lower concentrations to higher concentrations which make the zeolite amorphous. This phase transition has been attributed to the interaction between clusters throughout the zeolite framework. Even though the arrangements of the CdS clusters is not yet clearly understood, increase in the CdS concentration causes a build up of stresses to a critical point beyond which the crystalline structure collapses; CdS crystallinity is conserved for all concentrations used. Photothermal techniques allowed us to obtain the energy band-gaps, $E_g$, of the samples and their thermal properties: diffusivity, $\alpha$, heat capacity, $C_p$, and conductivity, $k$, as a function of the CdS concentration (embedded in the zeolite framework). All the curves obtained (for $E_g$, $\alpha$, $k$ and $\rho C_p$) showed a maximum for a critical concentration of 31.4 wt.% of CdS. The $E_g$ behaviour is explained by considering that increasing the semiconductor concentration causes
also an increase in the interaction between CdS clusters (which gives origin to the superclusters). With corresponding lattice shrinkage, a rise in $E_p$ is observed until a maximum is reached. Beyond this point, the structure of the zeolite becomes amorphous and $E_p$ is that of bulk CdS. The maximum in the thermal parameters $\alpha$ and $k$ is due to increasing CdS concentration, while decreasing porosity eases the heat flux through the material. In this way, $\alpha$ and $k$ increase as the concentration increases, while the zeolite framework is preserved. It is evident that when the zeolite becomes amorphous the heat flow diminishes. The maximum in the heat capacity $C_p$ is evidence of the crystalline-to-amorphous phase transition of the zeolite.

This work was partially supported by CONACyT-México. The authors are grateful to Ing. M. J. Guerrero, A. Buendia and A. Castillo for their technical assistance.

References


Paper 5/07953E; Received 6th December, 1995