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Synthesis and Characterization of III-V Semiconductor Clusters: GaP in Zeolite Y

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Size quantization effects observed in small semiconductor clusters are currently of great interest for potential nonlinear optic and photocatalytic applications.¹⁻¹¹ While materials based on II-VI semiconductors have been extensively studied, the preparation of III-V size quantized semiconductors has been hampered by the much less-developed solution state chemistry in such systems.¹² With the use of inclusion chemistry, we have succeeded in preparing small clusters of GaP in a crystalline, periodic environment of well-defined size and shape (zeolite Y).

The reaction $(\text{Me})_3\text{Ga} + \text{PH}_3 \rightarrow 3\text{CH}_4 + \text{GaP}$ was carried out within the pores of Na⁺/H⁺ exchanged zeolite Y, by using various loadings of (Me)₃Ga and different reaction temperatures and times with PH₃. The synthesis is accomplished by vapor transfer of (Me)₃Ga into dry zeolite and slowly warming to room temperature, resulting in CH₄ evolution due to the reaction of (Me)₃Ga with Brønsted acid sites in the zeolite. Excess (Me)₃Ga and CH₄ are

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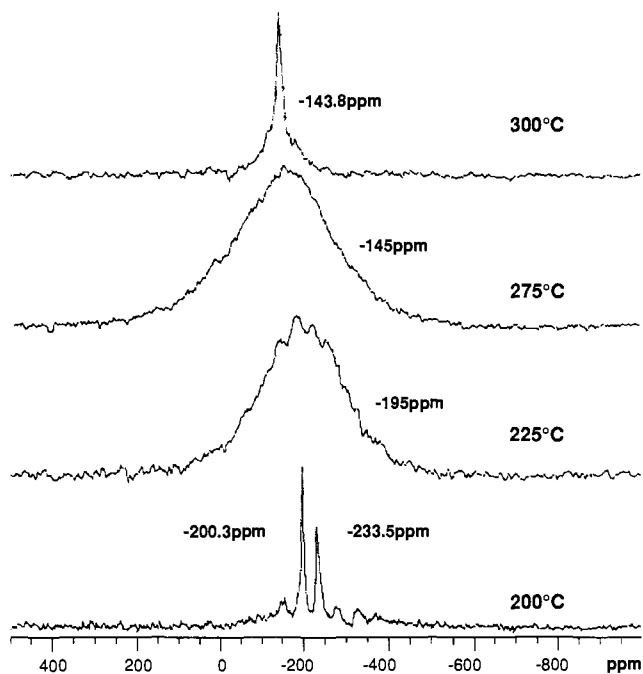


Figure 1. 121.65 MHz ³¹P MAS NMR of microdisperse GaP in zeolite NaY. The numerals indicate the different temperatures of PH₃ treatment of the (Me)_{3-x}Ga loaded samples. All samples contain comparable amounts of phosphorus. Chemical shifts (in ppm, vs 85% H₃PO₄) are indicated in the figure. For the broad signals, the center of gravity is calculated from the first moment. Minor unlabeled peaks represent spinning sidebands.

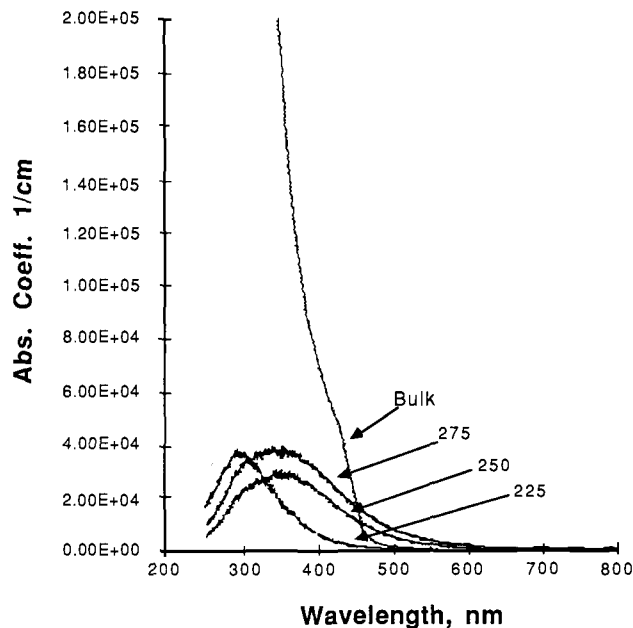


Figure 2. UV-vis spectra of bulk GaP and GaP included in zeolite NaY, treated at 225, 250, and 275 °C in PH₃.

pumped off at room temperature, and the (Me)_{3-x}Ga loaded zeolite is treated with an excess of PH₃ for several hours at a series of temperatures between room temperature and 400 °C. The product is cooled in vacuum and handled in an inert atmosphere thereafter. The color of samples vary with treatment temperature (white below 200 °C and yellow to orange between 200 and 300 °C), and this change is reflected in the systematic trend seen in the UV-vis spectra. Optical spectra in Figure 2 show a pronounced peak at 290 nm for the low-temperature sample and at 350 nm for the high-temperature samples. These absorption peaks are blue shifted from the band gap of bulk GaP (direct 466 nm, indirect 546 nm). We also note that the 250 °C and 275 °C samples absorb to the red of bulk GaP. This may be due to the

transformation of an indirect to direct gap, which could be induced by relaxation of the k-selection rule in the quantum confinement regime. This interesting explanation remains to be proven since the possibility of impurity absorption in the tail region has to be rigorously excluded. Bulk chemical analyses (Galbraith Labs., Knoxville, TN) demonstrate that at shorter contact times of PH_3 (3 h or less) the Ga:P ratio is large (11:1, at 300 °C, 3 h) but at longer times (12 h) the ratio is reduced (0.4:1), indicating the presence of unreacted $(\text{Me})_{3-x}\text{Ga}$ or phosphorus, respectively. X-ray diffraction patterns (both from a lab source and the synchrotron) of samples treated at 300 °C and below show no reflections other than those of the zeolite host (with greatly modified relative intensities due to the inclusion); however, at PH_3 treatment temperature of 400 °C, bulk GaP can be identified.¹³

For lower annealing temperatures, the formation of microdisperse GaP was monitored by ^{31}P MAS NMR. Figure 2 shows the spectra for four separate samples which had been exposed to $(\text{Me})_3\text{Ga}$ by vapor transport and treated for 3 h in PH_3 at various temperatures. The sample annealed at 200 °C shows several distinct signals (attributed to molecular precursor complexes) superimposed on a broad resonance (assigned to microdisperse GaP). As the temperature is increased, the sharp peaks disappear, and only the broad resonance, dominated by a distribution of isotropic chemical shifts, remains. Most notably, the center of gravity of the broad resonance is found significantly upfield with respect to bulk GaP (-143 ppm vs 85% H_3PO_4)¹⁴ and gradually shifts towards that position with increasing annealing temperature. For the 300 °C sample, the signal has sharpened significantly and resembles that of bulk GaP,¹⁴⁻¹⁶ whereas the NMR spectrum of the 400 °C sample confirms the formation of the bulk material.

The EXAFS results,¹⁷ for a sample treated at 300 °C with a short PH_3 contact time (i.e., 3 h), confirm the formation of small GaP clusters most likely located in the supercages of the zeolite.¹⁸ Several different shells can be identified by fitting with adequate reference compounds. Ga is present in two distinct coordination environments. About 70% of the Ga is coordinated to the zeolite framework with an average Ga-O bond length of 2.04 Å. A peak at about 2.5 Å (uncorrected for phase shift) is interpreted as the corresponding Ga-Si/Al scattering from the host lattice. The second environment consists of GaP which is indicated in the EXAFS spectrum and the XANES (X-ray absorption near edge spectroscopy) region of the absorption edge. Three coordination shells of GaP were identified by the fitting procedure: a Ga-P shell at 2.37 Å (coordination number = 0.9), a Ga-Ga shell at 3.85 Å (CN = 1.1), and a second Ga-P contribution at 4.56 Å (CN = 1.5). These bond distances are consistent with those in bulk GaP. The small coordination numbers derived from the fit and the absence of any additional GaP shells indicate the formation of clusters with a size between 10 and 12 Å. Further EXAFS and X-ray diffraction experiments are in progress to better elucidate the structural nature of the species which are formed.

The results thus far indicate that we are able to synthesize small clusters of GaP within the pores of a zeolite and that we can change the optical properties by varying the synthetic conditions. The NMR results confirm the postulated chemistry and the suitability of this technique to monitor the transformation of microdisperse GaP during the synthesis. In conjunction with the UV-vis results and by analogy with the ^{77}Se NMR studies of colloidal CdSe ¹⁹ we interpret the chemical shift trend observed in Figure 2 in terms of a systematic change in the average excitation energy of Ramsey's paramagnetic chemical shielding contribution as a result of size quantization.²⁰ We therefore propose that, with proper calibration, solid-state NMR chemical shifts can be used to measure the average cluster sizes of such systems.

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Supplementary Material Available: Figure showing an EXAFS spectrum of sample GaP/NaY 300 °C, magnitude and imaginary parts, Fourier transformed with k^3 between 2.8 and 13.1 Å⁻¹ (1 page). Ordering information is given on any current masthead page.

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Trapping of the Low-Valent Nitrene Complex $(\text{CO})_5\text{W}=\text{NPh}$ with PPh_3 . Formation of the Phenylnitrene Transfer Product $\text{PhN}=\text{PPh}_3$

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We recently reported the formation of the zwitterion $(\text{CO})_5\text{WNPhNPhC}(\text{OCH}_3)\text{CH}_3$ (**1**) as an isolable intermediate in the metathesis reaction of $(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)\text{CH}_3$ with photochemically generated *cis*-azobenzene.¹ Decomposition of **1** under thermal or photochemical conditions resulted in formation of the organic metathesis product $\text{PhN}=\text{C}(\text{OCH}_3)\text{CH}_3$ ² and other compounds apparently derived from the low-valent tungsten nitrene complex $(\text{CO})_5\text{W}=\text{NPh}$ (**2**).^{3a} Many imido complexes have been reported in the literature.^{4,5} However, although species such as the low-valent doubly bonded **2** have been invoked in reaction mechanisms,³ they have not been directly observed. We now report that thermal decomposition of **1** in the presence of PPh_3 results in the trapping of nitrene complex **2** as its phosphine

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(16) The corresponding ^{69}Ga NMR signals in the disordered low-temperature samples are broadened beyond detectability due to quadrupolar coupling. The 300 °C sample exhibits a weak ^{69}Ga MAS NMR signal, which is broadened and shifted due to second-order quadrupolar perturbations, whereas the NMR spectra of the 400 °C sample confirm the formation of the bulk material.

(17) EXAFS measurements were performed at the National Synchrotron Lightsource at Brookhaven National Laboratories on beamline X-11A with a stored electron energy of 2.5 GeV and ring currents between 100 and 130 mA. Data were collected at the Ga K-edge of 10367 eV at ~100 K in transmission mode using a Si(111) channel-cut monochromator. Harmonic contributions were eliminated by detuning the maximum signal ~30%. Samples and reference compounds were embedded in a 1:1 mixture of icosane/octadecane and stored under nitrogen. Thickness of materials was calculated to give a total absorption $\mu_x < 2.5$, and data were collected up to 1000 eV over the absorption edge with two scans/sample. Analyses were carried out according to published procedures. (See: Lee, P. A.; Citrin, P. H.; Eisenberger, P.; Kincaid, P. M. *Rev. Mod. Phys.* **1981**, *53*, 769.)

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