Structure of selenium clusters in the framework of zeolite Nd-Y

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(Received 24 November 2008; published 14 April 2009)

A detailed model for the structure of selenium clusters in the framework of zeolite Nd-Y has been determined by x-ray powder diffraction. The model, which is consistent with previous theoretical and Raman studies, was determined by analysis of the data. We propose the coexistence of isolated Se 12-membered rings and Se nanoclusters made out of these 12 rings in the α cages of zeolite-Y. Our x-ray data also show substantial diffuse scattering associated with considerable disorder within the pores of the Se/zeolite-Y system. Our work on these systems has made use of a total Rietveld refinement to obtain the *average* nanomolecular structure.

DOI: 10.1103/PhysRevB.79.132104 PACS number(s): 61.46.Df, 61.05.C−, 78.70.Ck, 82.75.Vx

I. INTRODUCTION

Nanostructured semiconductors possess novel properties due to the spatial confinement of charge carriers (electrons) in discrete energy levels. These nanostructures are of great interest for a variety of potential electronic, photochemical, and nonlinear optical applications.[1,2] Fabrication of nanoclusters in organized frameworks, such as in zeolites, is a well-known strategy to produce nanoclusters with a narrow size distribution.[3] A number of technologically important metals and semiconductors such as CdS(Se), Rb-Se, Cs-Se, Se, Pt, PbI_2, and HgSe (Refs. 3–10) have been studied in the confined environments of zeolite frameworks. Due to the low melting point and the variety of applications in the industry, selenium is one of the most extensively studied semiconductor materials in host frameworks.

In particular Se in zeolite Nd-Y, which is the system under investigation here, has previously been studied by Armand *et al.*[7] in a very nice x-ray anomalous scattering study in which they could remove the framework atoms and obtained a differential pair-correlation function from which they rationalized the Se structure within the pores. However, as we shall show, this analysis was distinctly different from our direct results. In addition, we provide structural coordinates that are not accessible to their *r*-space method.

The short-range ordering of the guest molecules in zeolite/nanocluster systems on the atomic scale, and distortions of the zeolite framework in the vicinity of these molecules, which is observed in the form of diffuse scattering in between the Bragg peaks of the x-ray-diffraction (XRD) pattern, makes the structural analysis difficult. Conventional powder-diffraction techniques, such as the Rietveld method,[11–13] fail to obtain structural information from this issue. In such situations, the atomic pair distribution function (PDF) technique[14–17] can provide very useful information regarding short- and long-range orders simultaneously. The PDF, sine Fourier transform of the total (Bragg+diffuse) diffraction pattern, is a two-point correlation function which can be theoretically generated from a structural model.

In this study, Se nanoclusters were synthesized in the 13 Å diameter sodalite cages of zeolite Nd-Y and the *average* structure of the Se/zeolite system was determined by performing a Rietveld[12,13] refinement on powder-diffraction data. As a result, a detailed *average* structural model is presented for the Se/Nd-Y system. Our results are favorably compared with the Raman studies of Poborchii *et al.*[18] and the theoretical studies of Demkov and Sankey[19] on Se/zeolite-A system (the zeolite-A framework contains ~11.4 Å diameter cages). Pronounced diffuse scattering present in our x-ray-diffraction pattern will also be discussed in terms of intramolecular disorder, another feature of our data (and of the HgSe data[3,10]).

II. EXPERIMENTAL

The hydrated form of zeolite Na-Y, $Na_{56}(H_2O)_xSi_{136}Al_{56}O_{384}$ (from Zeolyst), was used for our study. An Nd^{3+} ion exchange was performed to remove the extraframework cations (Na^+) from zeolite α cages [sites SI, SIV, and SV (Ref. 20)] and limit the resulting Nd^{3+} to SI and SI′ sites[20] according to the method described by Abeykoon *et al.*[3] The Se nanoclusters were then synthesized in dehydrated zeolite cages by chemical-vapor deposition (CVD) (Ref. 3) at 360 °C. The XRD data were collected on a Rigaku SmartLab multipurpose diffractometer using a flat sample plate in reflection geometry. Samples were exposed to atmospheric conditions before the data collection. A color change of the samples, from bright orange to dark orange (a redshift), was observed upon the exposure to the atmospheric conditions. In agreement with Poborchii *et al.*,[18] this redshift can be associated with formation of larger clusters after the diffusion of Se from interior of the cages to the surface of the cages.

III. DATA AND ANALYSIS

Figure 1 shows the XRD data for our sample. Note that the (+) represents the observed data and the line represents the Rietveld fit to the data to be discussed. Diffuse scattering between the Bragg peaks was fitted using a Chebyshev polynomial and it was subtracted for the Rietveld refinement.

The Rietveld refinement was performed on XRD data using the GSAS/EXPGUI (General Structure Analysis System)[21,22] computer package. A pseudo-Voigt function and

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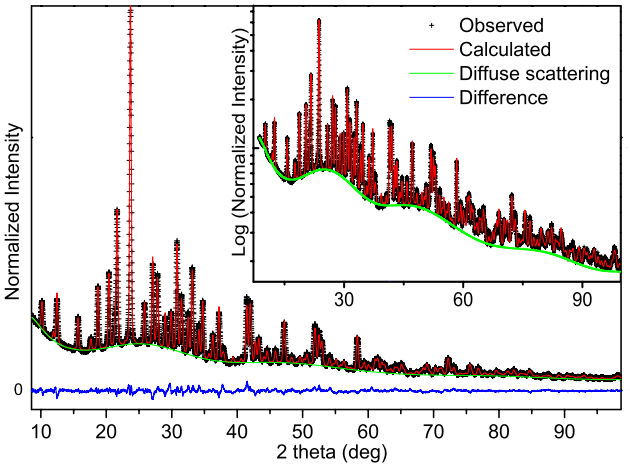

FIG. 1. (Color online) (a) The Rietveld fit to the powder pattern of Se/Nd-Y. Goodness of fit $\chi^2=9.001$. Plots show the observed (+) and calculated (−) powder patterns. A difference curve is shown at the bottom of the diagram. The inset shows a logarithmic-scale version of the graph (Bragg and diffuse scattering). Note that the diffuse scattering was subtracted for the Rietveld refinement. The refined lattice parameter $a=b=c=24.6678(4)$ Å.

a shifted Chebyshev polynomial were used to refine the peak profile and the background. respectively. Gaussian and Lorentzian parameters[11] of the profile, GU, GV, GW, LX, and LY, were refined after refining the zero shift, lattice parameter, and the background function. Then the atomic coordinates, occupation numbers, and the isotropic thermal displacement parameters (U_{iso}) were refined. At the last stage of the refinement, all the parameters (profile and structural) were refined simultaneously to obtain optimal fits and satisfactory structural models. Appropriate constraints (thermal, compositional, and bond length) were applied depending on the Se concentration and its expected structure. Compositional constraints were applied based on the reaction stoichiometry which agrees with the results of chemical analysis. Bond-length constraints were applied on Se atoms, giving them a 1% ($\sigma=0.01$) shift.

According to the results of the Rietveld refinement, we propose the existence of isolated Se 12-membered rings and Se clusters made out of these 12-membered rings in the α cages of the zeolite Nd-Y. These Se 12-membered rings agree quite well with the experimental studies of Poborchii *et al.*[18] and the theoretical studies of Demkov and Sankey[19] on the Se/zeolite-A system (the zeolite-A framework contains ~11.4 Å diameter cages). The refined average atomic coordinates, occupancies, and U_{iso}'s are presented in Table I. The higher U_{iso}'s of the Se sites must be associated with the statistical disorder at these sites due to the substitutional and displacive disorder. The coordinates for the Se sites can show $\pm(2-3)\%$ difference depending on the amount of absorbed water in zeolite, but the basic symmetry of the nanocluster will remain intact and there is no aspect of the nanocluster which breaks the zeolite host symmetry (no new Bragg peaks). Since zeolite-A (Ref. 19) has smaller cages than Nd-Y, it may provide Se 12 rings an environment similar to the large Nd-Y cage containing H_2O molecules. These H_2O molecules can heavily influence the atomic arrangement of Se in Nd-Y cages. We have observed water molecules at the center of these 12 rings by a difference Fourier synthesis. A completely different structure was refined for the data collected at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, on Se/Nd-Y *dry* samples sealed in capillaries, using a cylindrical geometry, and these results will be presented in a separate paper.

Even though there are 8α cages in the Nd-Y unit cell, all of them cannot be completely filled according to the reaction

TABLE I. Refined atomic coordinates, thermal parameters, and occupancy of the Se/Nd-Y structure. Standard deviations of 1-σ are indicated in parentheses.

Name	x/a	y/b	z/c	U_i/U_e*100	Mul.[a]	Occ.[b]
Se1	0.3038(2)	0.3038(2)	0.3038(2)	17.85(4)	32	0.2648(2)
Se2	0.1014(1)	0.4499(2)	0.1014(1)	17.85(4)	96	0.2269(1)
Se3	−0.4596(4)	0.8125(2)	−0.0625(2)	17.85(4)	96	0.1250(1)
SI	0.9451(4)	0.1279(4)	0.0346(4)	2.05(4)	192	0.7268
Al	0.9452(4)	0.1279(4)	0.0346(4)	2.05(4)	192	0.2731
O3	0.8900(1)	0.0000	0.1030(1)	1.15(6)	96	1.0000
O4	−0.0008(1)	−0.0008(1)	0.1351(2)	1.15(6)	96	1.0000
O5	0.9708(2)	0.0826(1)	0.0826(1)	1.15(6)	96	1.0000
O6	0.9309(2)	0.0664(1)	0.1836(1)	1.15(6)	96	1.0000
Nd1	0.0000	0.0000	0.0000	3.95(5)	16	0.1200
Nd2	0.0679(5)	0.0679(5)	0.0679(5)	3.95(5)	32	0.6584
H2O1	0.0293(3)	0.5489(4)	0.0293(3)	80.00(17)	96	1.0000
H2O2	7.0933	7.0933	7.0933	80.00(17)	32	0.0000
H2O3	0.4448(1)	0.9011(2)	0.3053(1)	80.00(17)	96	0.3483(2)

[a]Site multiplicity.
[b]Site occupancy.

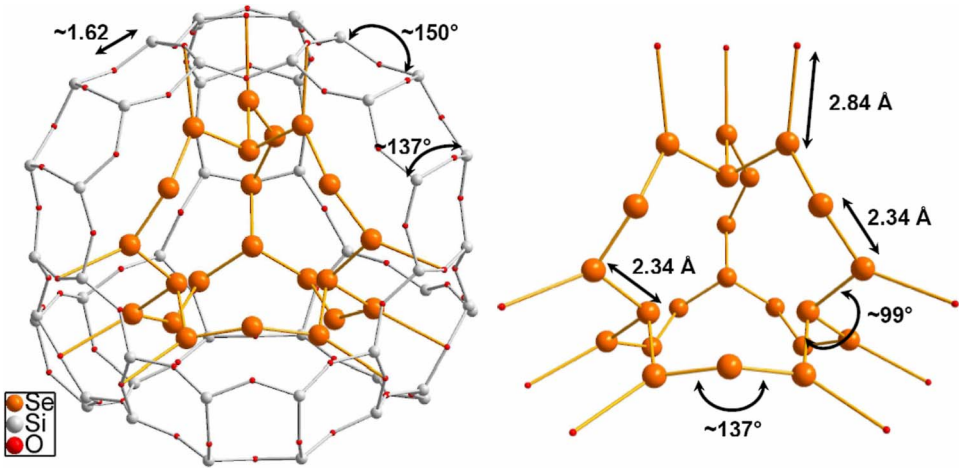

FIG. 2. (Color online) Proposed structural model for the Se nanocluster (right), and the orientation of it in the Nd-Y α cage (left).

stoichiometry. The vacancies which can exist in the filled cages can effectively contribute to statistical and displacive disorder associated with the Se sites. This statistical disorder gives rise to the diffuse scattering underlying the Bragg peaks. Furthermore, the possible local framework distortions of the Se nanoclusters can also contribute to diffuse scattering. The Rietveld fit and the proposed structural model for the refined coordinates (Table I) are given in Figs. 1–3, respectively.

We compare our Se 12 rings with the findings of Poborchii *et al.*[18] and Demkov and Sankey.[19] Both zeolite-Y and -A are cubic crystal systems with 13 Å (Ref. 20) and 11.4 Å (Ref. 18) diameter supercages, respectively. However, they show different framework symmetries, $Fd-3m$ for zeolite-Y and $Pm-3m$ for zeolite-A. Since the supercages of zeolite-Y are larger than the supercages of zeolite-A, more than one Se 12 rings may exist in one supercage to form *average* nanoclusters. We do not deny the possibility of the existence of incomplete clusters (deviations from the *average*) may be present in zeolite supercages and individual clusters may certainly show substantial deviations from the *average* refined model. Some of the cages in the zeolite-Y framework may not be completely filled and they may contain isolated Se 12 rings or Se chains with few atoms. Our intention is to present the refined coordinates and occupancies of the possible Se sites in zeolite cages (Table I) with the most feasible *average* structural model for the Se/Nd-Y system. Distances and angles in the refined Se 12-ring structure are presented in comparison with the results of Poborchii *et al.*[18] and Demkov and Sankey[19] in Table II. Obviously due to the large cage size, different framework symmetries, and the number of Se atoms in a single cage, Se 12 rings in Nd-Y supercages can show differences in bond lengths and angles from the Se 12 rings in zeolite A (Table II). We should also note the fact that Se can form a variety of different structures in different size zeolite cages. This diversity has been clearly shown in zeolites in the literature.[6,18,23,24] However, the Se 12 rings presented in this Brief Report are remarkably close to the previous findings in zeolite-A.

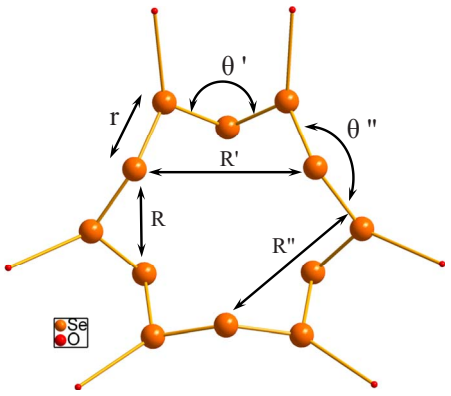

FIG. 3. (Color online) Se 12 rings which constitute the basic nanocluster in Fig. 2.

IV. CONCLUSION

The average structure of the Se/zeolite Nd-Y system has been determined. The possibility of the existence of Se 12-membered rings in zeolite-Y cages was clearly shown. Our results are consistent with the previous studies of Poborchii *et al.*[18] and Demkov and Sankey[19] on the Se/zeolite-A system. Through this work, we have identified a different molecular Se structure from the known structures that Se can form in confined environments and have illuminated this issue through the evaluation of $\langle U_{iso} \rangle$ for Se which are ~0.85 Å. This large value is clearly associated with the thermal or static displacements of a distribution of Se distances within the nanocluster.

TABLE II. Comparison of the bond lengths and bond angles of our Se 12 rings with those in previous works.

Parameter	This work	Poborchii *et al.*[a]	Demkov and Sankey[b]
r (Å)	2.33	2.32	2.313
R (Å)	3.59	3.706	3.748
R' (Å)	4.99	4.620	4.778
R'' (Å)	4.98	4.744	4.823
θ'	99	106	108

[a]Reference 18.
[b]Reference 19.

ACKNOWLEDGMENTS

We thank the DOE BES on Contract No. DE-FG02-04ER46160 for their extended financial support of this work and the Robert A. Welch Foundation. This work was partly supported by the State of Texas through the Texas Center for Superconductivity at the University of Houston. We thank Rigaku Americas Corporation for the use of their instruments. We also thank A. Demkov at the University of Texas at Austin for his comments.

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