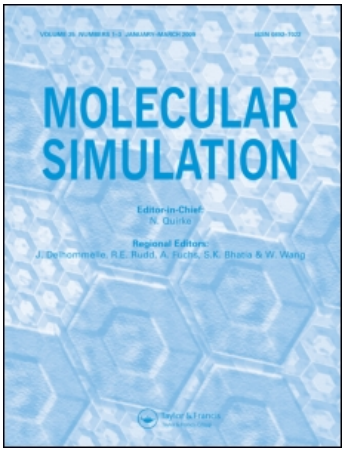

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Atomic-scale structure of nanocrystals by the atomic pair distribution function technique

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Atomic-scale structure of nanocrystals by the atomic pair distribution function technique

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The approach of the atomic pair distribution function (PDF) technique to determine the atomic-scale structure of nanocrystalline materials is introduced and illustrated with results of studies on V_2O_5 nanotubes and clusters of Cs atoms intercalated inside the pores of the zeolite ITQ-4. We find that V_2O_5 nanotubes are built of double layers of V-O_5 and V-O_4 units. Inside the channels in ITQ-4 Cs atoms are found to assemble in short-range ordered zigzag chains.

Keywords: Structure determination; X-ray diffraction; Bragg peaks; V_2O_5 nanotubes

1. Introduction

Knowledge of the atomic-scale structure is an important prerequisite to understanding and controling the properties of materials. In the case of crystals it is obtained solely from the Bragg peaks in their diffraction pattern and is given in terms of a small number of atoms placed in a unit cell subjected to symmetry constraints. However, many materials of technological importance, including nanocrystalline materials, do not possess the long-range order of conventional crystals and often it is this deviation from perfect order that makes them technologically and/or scientifically important. The diffraction patterns of such materials show only a few Bragg peaks and a pronounced diffuse component. This poses a real challenge to the usual techniques for structure determination. The challenge can be met by employing the so-called atomic pair distribution function (PDF) technique. The frequently used atomic PDF, $G(r)$, is defined as $G(r) = 4\pi r[\rho(r) - \rho_0]$, where $\rho(r)$ and ρ_0 are the local and average atomic number densities, respectively. It peaks at real space distances where the local atomic number density deviates from the average one, i.e. where most frequent interatomic distances occur, and thus reflects the structure of materials. The PDF $G(r)$ is the sine Fourier transform of the so-called total scattering structure function, $S(Q)$,

$$G(r) = \frac{2}{\pi}\int_{Q=0}^{Q_{\max}} Q[S(Q) - 1]\sin(Qr)\mathrm{d}Q, \qquad (1)$$

where Q is the magnitude of the wave vector. The structure function $S(Q)$ is related to the coherent part, $I^{\mathrm{coh}}(Q)$, of the powder diffraction intensities as follows:

$$S(Q) = \frac{1 + \left[I^{\mathrm{el.}}(Q) - \sum c_i |f_i(Q)|^2\right]}{\left|\sum c_i f_i(Q)\right|^2}, \qquad (2)$$

where c_i and f_i are the atomic concentration and atomic scattering factor, respectively, for the atomic species of type i [1]. As can be seen the PDF is simply another representation of the diffraction data. However, exploring the experimental data in real space is advantageous, especially in the case of materials with reduced long-range order such as nanocrystals. First, as equations 1 and 2 imply the *total*, not only the Bragg diffracted, intensities contribute to the PDF. In this way both the *average*, long-range atomic structure, manifested in the sharp Bragg peaks, and the *local*, non-periodic structural features, manifested in the diffuse components of the diffraction pattern, are reflected in the PDF. Note the conventional crystallographic studies take only the Bragg peaks into account. Second, the PDF is obtained with no assumption of periodicity. Also, it is barely affected by diffraction optics and experimental factors since these are accounted for in the step of normalizing the raw diffraction data and converting it to PDF data. This renders the PDF a structure-dependent quantity giving directly relative positions of atoms in materials and enables convenient testing and refinement of structural models. Here we demonstrate how the PDF technique works by

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employing it to determine the structure of two nanocrystalline materials: V_2O_5 nanotubes and nanoscale clusters of Cs atoms.

Crystalline vanadium pentoxide, V_2O_5, is an important technological material widely used in applications such as optical switches, chemical sensors, catalysts and solid-state batteries [2]. The material possesses an outstanding structural versatility and can be manufactured into nanotubes that have many of the useful physicochemical properties of the parent V_2O_5 crystal significantly enhanced. For example, the high specific surface area of the nanotubes make them even more attractive as positive electrodes in secondary Li batteries [3]. Also, the nanotubes show significantly increased capability for redox reactions [4]. The structure of the nanotubes is an important issue since good knowledge of it is a key to understanding a material's properties.

Cs-intercalated $Si_{32}O_{64}$ belongs to the class of novel low-dimensional electron systems known as "electrides" [5]. In these materials a low-density gas of correlated electrons is confined in the cavities of an inert host and coexists with a nanoscale array of alkali ions that provide charge balancing. The confined electron gas exhibits Mott insulation behavior and Heisenberg antiferromagnetism. Recently, the first inorganic electride that is stable at room temperature has been synthesized by intercalating Cs into the zeolite ITQ-4 ($Si_{32}O_{64}$). Here we use the PDF technique to find the arrangement of Cs^+ ions inside the nanopores of ITQ-4.

2. Experimental

Vanadium oxide nanotubes were synthesized by mixing crystalline vanadium oxide and dodecylamine in absolute ethanol, stirring in air for two hours and then hydrolyzing with osmosis reversed water. After aging for 3 days and hydrothermal treatment in an autoclave at 180°C for 7 days, a black precipitate was obtained. The product was washed with water, ethanol, hexane and diethyl ether to remove the unreacted amines and decomposed products, and dried overnight under vacuum at 80°C to prevent oxidation of vanadium +4 to +5. Thus prepared nanotubes and crystalline V_2O_5 were sealed between Kapton foils and subjected to X-ray diffraction experiments.

Electrides $Cs_xSi_{32}O_{64}$ ($x = 3.6$, 4.6) were prepared by mixing dehydrated $Si_{32}O_{64}$ and a weighted amount of cesium metal in sealed borosilicate flasks and heating to 60°C. The amount of absorbed Cs was determined by collection of hydrogen evolved upon reaction with water, and by titration of the CsOH formed. As prepared electrides and pristine ITQ-4 were sealed in capillaries and subjected to diffraction experiments.

The diffraction experiments on the vanadium oxide nanotubes were carried out at the beamline 1-ID at the Advanced Photon Source, Argonne National Laboratory and those on the electrides at the beam line X7A of the NSLS, Brookhaven National Laboratory. Several runs were conducted with each of the samples measured and the resulting XRD patterns were averaged to improve the statistical accuracy and to reduce any systematic effect due to instabilities in the experimental set-up. The raw diffraction data were corrected for the decay of the incoming synchrotron radiation beam, for background and Compton scattering, for sample absorption, normalized, i.e. converted into electron units, and then reduced to structure functions $S(Q)$ and the corresponding PDFs $G(r)$. All data processing was done using the program RAD [6].

3. Results and discussion

Vanadium oxide nanotubes are typically up to 15 μm long and have inner diameters between 5 and 15 nm while the outer diameters range from 15 to 100 nm. Their walls consist of several vanadium oxide layers as can be seen in figure 1. The lack of long-range order due to the curvature of the tube walls has a profound effect on the diffraction pattern of the materials. While the diffraction pattern of crystalline vanadium oxide shows sharp Bragg peaks [see figure 2(b)] that of the nanotube counterpart shows a pronounced diffuse component and only a few Bragg peaks [see figure 2(a)]. This renders the traditional techniques for structure determination inapplicable. However, the atomic PDF of nanocrystallineV_2O_5 obtained from the diffraction data of figure 2(a) is rich in distinct, structure related features (see figure 3) and lends itself to structure determination, just like the PDF of a crystal does. The only difference is that the PDF of a crystal persists to very high real space distances [see figure 3(a)] as it should be with a material exhibiting a long-range order. The PDF of nanocrystal decays to zero at much shorter interatomic distances [see figure 3(b)] due to the limited structural coherence in the material.

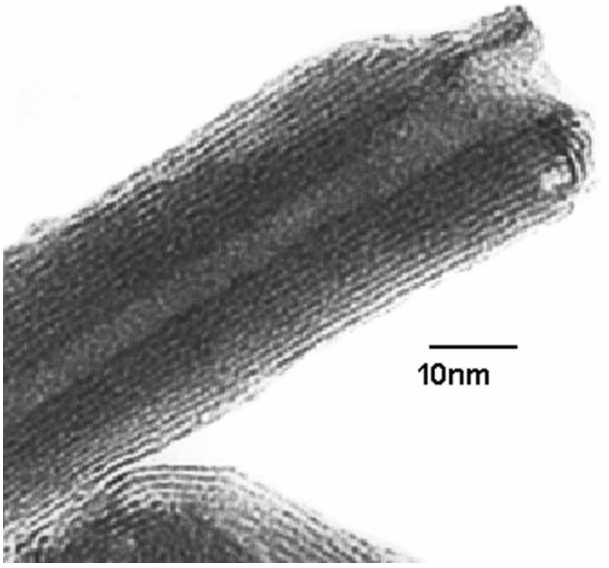

Figure 1. TEM image of vanadium oxide nanotubes used in the present study.

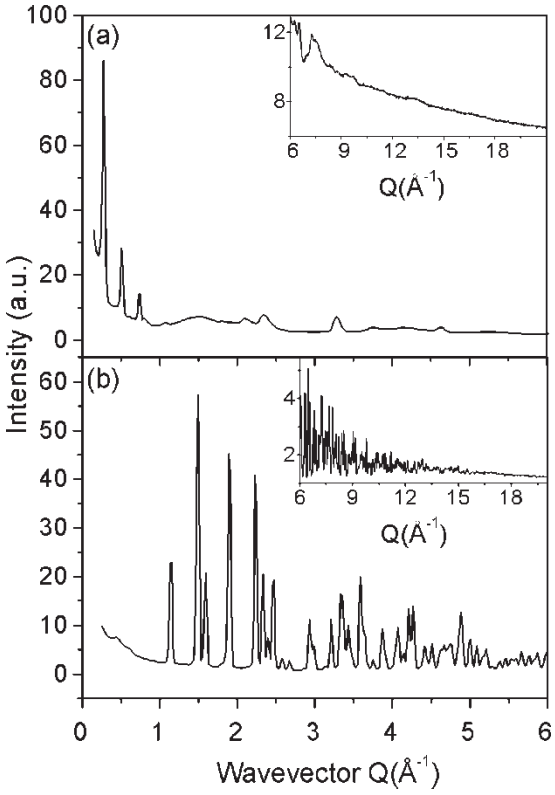

Figure 2. Experimental powder diffraction patterns for V_2O_5 nanotubes (a) and crystalline V_2O_5 (b). The high-Q portion of the patterns is given in the insets on an enlarged scale.

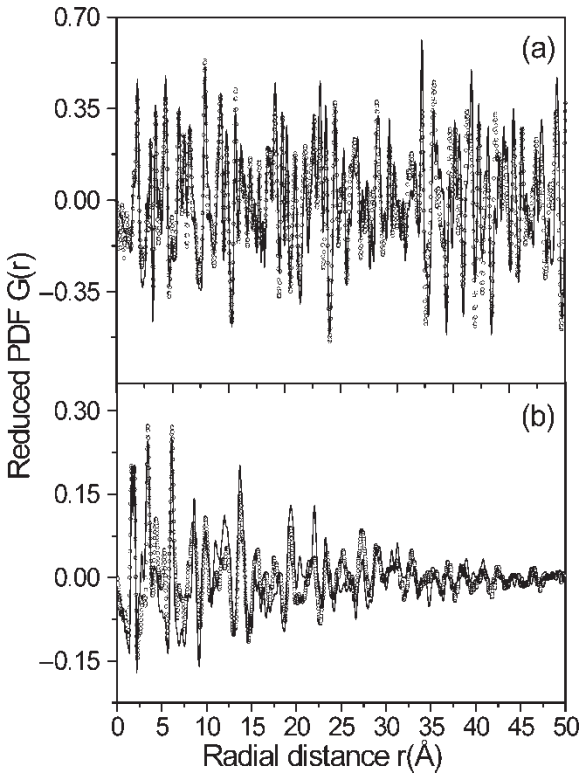

Figure 3. Comparison between experimental (circles) and model (solid line) PDFs for: (a) crystalline V_2O_5 and its well known orthorhombic structure [7], (b) V_2O_5 nanotubes and the triclinic $BaV_7O_{16}{\cdot}n\,H_2O$-type structure [9] refined against the experimental PDF data.

The well-known 16-atom unit cell of crystalline V_2O_5 [7] was fit to the experimental PDF observing the symmetry constraints of the *Pmmn* space group [see figure 3(a)]. The fit was done with the program PDFFIT [8]. The program employs a least-squares procedure to compare experimental and model PDFs calculated from a plausible starting model. In comparing with experiment, the model PDF is convoluted with *Sinc* function, $S(r) = \sin(Q_{\max}r)/r$, to account for the termination of the experimental data at $Q_{\max}$. The structural parameters of the model are adjusted until the best fit to the experimental PDF data is achieved. The current fit yielded the following cell constants for V_2O_5: $a = 11.498(3)$ Å, $b = 3.545(3)$ Å, $c = 4.345(3)$ Å. They are in good agreement with those obtained by traditional diffraction experiments: $a = 11.519$ Å, $b = 3.564$ Å, $c = 4.373$ Å [7]. The refined atomic positions are also in good agreement with previous results. The agreement well documents the fact that the atomic PDF provides a reliable basis for structure determination. Several structural models were attempted for the vanadium oxide nanotubes [9]. Best fit to the PDF data was achieved with a model based on a triclinic unit cell (S.G. $P\bar{1}$) with parameters $a = 6.020(3)$ Å, $b = 6.1305(25)$ Å, $c = 18.973(10)$Å, $\alpha = 93.235(9)°$, $\beta = 91.067(9)°$, $\gamma = 90.067(9)°$ [see figure 3(b)]. The model features the walls of the nanotubes as an ordered assembly of double layers of octahedral V-O_6 units with a small number of V-O_4 tetrahedra embedded into the layers [9]. The outcomes of the structure determination unambiguously show that even a nanocrystal with the complex morphology of vanadium pentoxide nanotubes possesses an atomic-scale structure very well defined on the nanometer length scale and well described in terms of a unit cell and symmetry. The new structural information allows to construct a real-size model of the nanotubes and understand their peculiar morphology [9].

Experimental powder diffraction patterns for the electride samples are shown in figure 4. Sharp Bragg peaks are present in the pattern of pristine $Si_{32}O_{64}$. The corresponding $G(r)$ (see figure 5) also features sharp peaks reflecting the presence of a long-range ordered network of Si-O_4 units in this crystalline material. As expected a model PDF calculated on the basis of the well-known 96-atom unit cell (S. G. I2/*m*) of $Si_{32}O_{64}$ [10] reproduces the experimental PDF data quite well. Bragg peaks in the diffraction patterns of the samples loaded with Cs are significantly attenuated and already at 2 Å^{-1} merge into a slowly oscillating diffuse component. This reflects the tendency of the zeolite host to become structurally disordered upon absorbing alkali metals. The significant diffuse scattering present in the diffraction patterns of $Cs_xSi_{32}O_{64}$ sample contains information about the atomic ordering of the intercalated Cs atoms. This information is lost in a usual crystallographic studies relying on Bragg scattering only but is taken into account in the corresponding atomic PDFs shown in figure 5. Careful inspection of the figure reveals a new feature at approximately 4 Å in the experimental PDFs of the Cs-loaded samples. The feature grows in line with

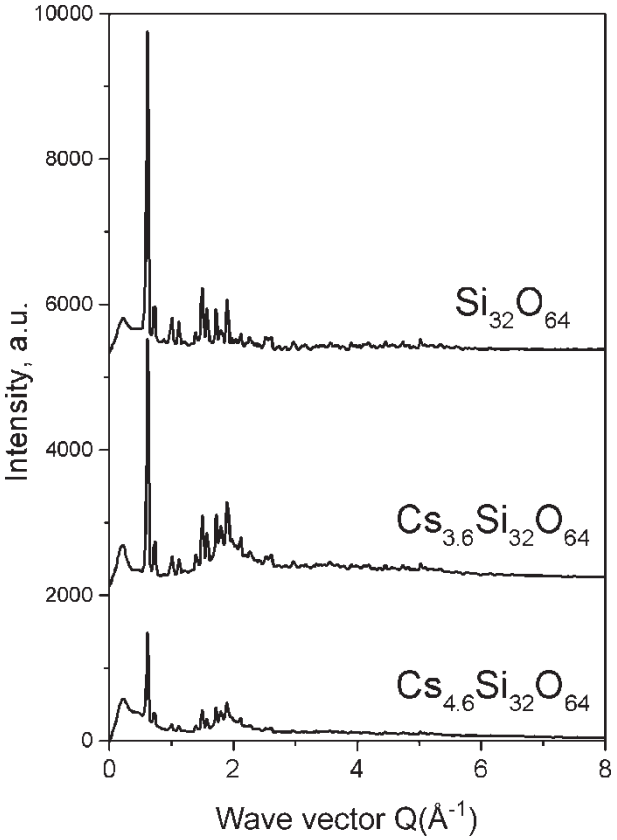

Figure 4. Experimental powder diffraction patterns for $Cs_xSi_{32}O_{64}$ ($x = 0,3.6, 4.6$).

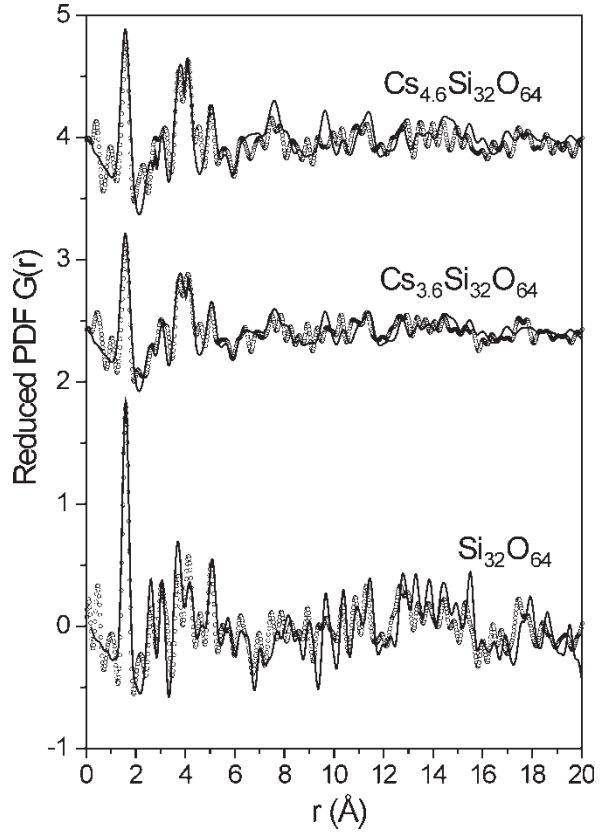

Figure 5. Experimental (circles) and model (line) PDFs for $Cs_xSi_{32}O_{64}$ ($x = 0,3.6, 4.6$). The experimental PDFs are obtained from the diffraction data of figure 4.

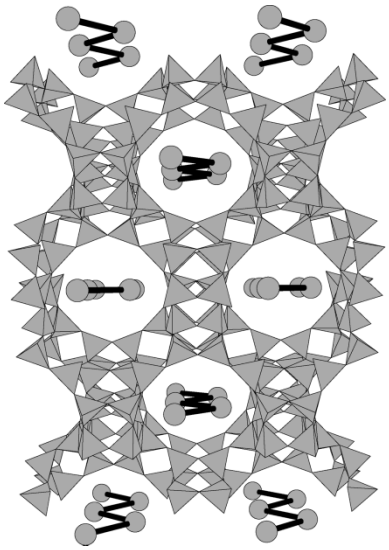

Figure 6. Fragment of the tetrahedral network in $Cs_xSi_{32}O_{64}$ with Cs ions (circles) in the nanopores assembled in zigzag chains.

the number of Cs atoms absorbed in the nanopores and thus can be unambiguously ascribed to atomic correlations involving Cs atoms. To identify the atomic ordering in the assembly of intercalated Cs atoms/ions we considered several structural models and tested them against the experimental PDFs. The models were constructed by placing cesium atoms and/or ions inside the nanopores in $Si_{32}O_{64}$ [11]. Best agreement with the experimental PDF data (see figure 5) was achieved with Cs^+ ions occupying positions 4*h* (1/2, 0.870(5), 0) and 4*g* (0, 0.370(5), 0) of the space group I2/*m*. According to the model, Cs^+ ions sit close to the walls of the sinusoidal channels in ITQ-4. Since the free space is limited, the intercalated metals are forced to come as close together as possible with increasing doping. As expected, this trend is opposed by an increase in the Coulomb repulsion between the positively charged Cs^+ ions. The balance is achieved when most of Cs ions occupy position 4*h* and 4*g* alternatively forming an assembly of short-range ordered zigzag chains as shown in figure 6. Such an extended cationic sublattice will necessitate that its counterpart, the confined electron gas, spreads out along the encapsulating channels rendering the material an electride.

4. Conclusion

In summary, the atomic-scale structure of nanocrystals and nanoscale clusters can be determined by employing a non-traditional experimental approach such as the atomic PDF technique. The technique relies on diffraction data obtained from the nanomaterial, it is sensitive to fine structural features and thus could differentiate between competing structural models. When coupled with extensive computer modeling it yields the atomic structure in terms of a small number of sensible parameters such as a unit cell and atomic coordinates. The new structural information may be used to explain and predict

the structure sensitive properties of the material. Thus the PDF technique has all the potential to become the tool for structure determination that is highly needed in the newly emerging field of nanoscience and technology.

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