319g Exploring the Natural Quantum Wires in Ets-4

Bilge Yilmaz, Juliusz Warzywoda, and Albert Sacco Jr.

Nanowires with diameters less than a few tens of nanometers (de Broglie wavelength) represent a link between molecular and solid state physics. These nanowires exhibit electrical, optical, magnetic and thermodynamic properties that are essentially related to their extremely small dimensions. These are called the "quantum size effects" and they are a consequence of the quantum confinement of the carriers. Nanowires with these enhanced transport properties due to quantum size effects are called quantum wires. Quantum wires have attracted attention due to the distinct features they offer for novel applications, especially in the fields of microelectronics, optoelectronics and non-linear optics. However, their fabrication still presents a problem of considerable technical complexity and cost. All of the conventional manufacturing techniques have severe size and geometry limitations since the dimensions processed are atomic-scale. ETS-4 is a small pore member of the Engelhard TitanoSilicate (ETS) family of mixed octahedral/tetrahedral microporous framework materials. The [TiO_6] octahedra are linked to form linear …Ti – O – Ti – O – Ti… chains, which are isolated from one another by siliceous matrix made of [SiO_4] tetrahedra. These chains exhibit quantum confinement effects and can behave as quantum wires. The …Ti – O – Ti – O – Ti… chains (quantum wires) in the ETS-4 structure are the thinnest wires that can be hypothesized since they are monatomic. In the absence of lattice defects these chains would have the same length as the crystals, however due to titanium vacancies, the chains are broken at random points in the crystals, resulting in the discontinuation of the quantum wires. The monolithic ETS-4 crystals with minimal intergrowth would have greater potential for quantum wire applications. Since the titania chains run along the longest axis of the crystal (b-axis, [010] direction) there is a need to control the morphology and size of ETS-4 crystals (in the b direction) as well as their lattice defects. ETS-4 crystals are usually obtained in the form of aggregates of highly intergrown plates, and synthesis of large single crystals of ETS-4 via direct hydrothermal methods is considered to be a challenge. A study was undertaken to examine the ways of controlling the quality of "natural" quantum wires in ETS-4, and the feasibility of orienting arrays of these quantum wires on substrates. Methods to control the morphology, crystal quality, relative amount of defects and degree of intergrowth of the ETS-4 product were developed. By adjusting the synthesis mixture composition (3.6 SiO_2 : 1 TiO_2 : 5.5 Na_2O : x H_2SO_4 : 230.2 H_2O, where x = 3.3 – 4.4), a gradual change of morphology of the ETS-4 product from spherulitic particles composed of submicron crystallites to monolithic crystals with rectangular prism morphology and micron sized dimensions was achieved. The X-ray powder diffraction and energy dispersive X-ray analyses suggested a smaller number of Ti vacancies (defects) in the monolithic crystals compared to the spherulitic particles. The largest dimension of these monolithic crystals (15-20 μm) coincided with the linear …Ti – O – Ti – O – Ti… chains running in the [010] direction. Effective strategies to directly control the size of monolithic ETS-4 crystals were developed, and large ETS-4 crystals with average dimensions ~10x200x20 μm were synthesized. To our knowledge, these are the largest ETS-4 crystals. Single crystal X-ray diffraction analysis demonstrated that these are single crystals with no detected intergrowth. Diffuse reflectance UV-visible (dr-UV-vis) spectroscopy studies demonstrated the blue shift of the optical band gap for the ETS-4 samples, which can be considered as the most straightforward verification of the quantum confinement in this structure. The dr-UV-vis and Raman spectra acquired for diverse ETS-4 samples exhibited different characteristics, which were hypothesized to be related to the quantum wire quality. Films of ETS-4 crystals oriented such that their b-axes are normal to the substrate plane ("b-out-of-plane" preferred crystal orientation) were grown in situ on various substrates. Since the …Ti – O – Ti – O – Ti… chains in ETS-4 crystals run in the [010] direction only, in principle, these films contain oriented arrays of quantum wires. These films can be utilized to test the potential of ETS-4 crystals as quantum wire components of thermoelectric and photovoltaic devices.