

# Hexagonally shaped Bi–Te nanocrystals and Bi or Bi–Te/ceramic nanocomposites of high metal loading from mixed-metal oxide precursors

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Bi or Bi–Te alloy/ceramic xerogel nanocomposites can be conveniently prepared at high total metal loading by hydrogen reduction of appropriate mixed-metal ceramic gels. Bi–Te nanoparticles having hexagonal shapes are formed and can be isolated free of the ceramic host matrix by chemical etching. These results serve as proof-of-concept (1) that nanostructured bismuth or bismuth alloy compositions can be synthesized in ceramic matrices at high loading utilizing selective reduction of mixed-metal oxide intermediates, and (2) that nanostructured bismuth phases in Bi/ceramic nanocomposites prepared *via* this synthesis strategy can be exposed through chemical etching of the ceramic phase.

## Introduction

There is much current interest in nanoscale Bi or Bi–Te alloys due to their semimetal and promising thermoelectric properties.<sup>1</sup> Nanoporous thin films of Bi have been obtained by spin-coating Bi(III) compounds onto solid supports followed by hydrogen reduction of the Bi(III) ions to Bi.<sup>2</sup> Bi nanoclusters are formed both in reverse micelles by borohydride reduction of surfactant-trapped Bi(III) compounds<sup>3</sup> and in the near-surface regions of silica glass rods by hydrogen reduction of *in situ* Bi(III) dopant ions.<sup>4</sup> Bi nanowires have been produced in the parallel, open channels of anodized alumina discs using either vapor-phase methods<sup>5</sup> or high-pressure, copper-metal-assisted impregnation of Bi melts.<sup>6</sup> Additional synthetic strategies for preparing practical quantities of nanostructured elemental Bi or Bi alloys are needed.

## Results and discussion

We now report a convenient chemical procedure for preparing nano-Bi or Bi–Te alloy/ceramic composites of nearly 50 wt% Bi using an *in situ*, bottom-up synthesis strategy.<sup>7</sup> In this approach, mixed-metal ceramics containing Bi(III) ions at high loading are produced using conventional sol–gel processing methods,<sup>8</sup> as shown in eqn. (1). Co-hydrolysis of silica or titania alkoxide precursors, **1a** (TMOS) or **1b**, with the known Bi(III) alkoxide, **2**,<sup>9</sup> leads to heterocondensation of the hydrolysis products and to formation of (Bi/Si) oxide or (Bi/Ti) oxide gels. Subsequent calcination affords porous mixed-metal oxide gels **3a** or **3b** as dry powders free of any residual organic groups. Thermal reduction of *in situ* matrix Bi(III) ions by hydrogen gas gives nano-Bi/silica or nano-Bi/titania composites, **4a** and **4b**, containing elemental Bi nanoclusters dispersed throughout the ceramic host matrix at arbitrary Bi loadings of 35 and 47 wt%, respectively.<sup>10</sup>

Transmission electron micrographs (TEM, Philips CM20T) of nanocomposites **4a** and **4b** reveal a high density of particles having average diameters of 10 and 5.3 nm, respectively, well dispersed throughout an amorphous ceramic gel matrix. The Bi nanoparticles lack definite shape but have sufficient crystallinity to give good contrast. Energy dispersive spectral (EDS) analysis of nanocomposites **4a** and **4b** reveals the presence of Bi and Si or Ti, as expected, and confirms the general homogeneity of these nanocomposites on the micron scale. A representative EDS spectrum of nanocomposite **4a** is shown in Fig. 1. Off-particle EDS spectra show no detectable amount of Bi within the ceramic phase indicating that essentially all of the Bi content is present within the observed nanoparticles.

Powder X-ray diffraction scans (XRD, Scintag X<sub>1</sub>  $\theta/\theta$  system) of nanocomposites **4a** and **4b** from 10–50° in  $2\theta$  show amorphous scattering from the ceramic gel component along with the (012), (104), (110), (015), (006) and (202) diffraction peaks known for bulk Bi metal. An XRD scan of nanocomposite **4b** along with the known line pattern of pure Bi is shown

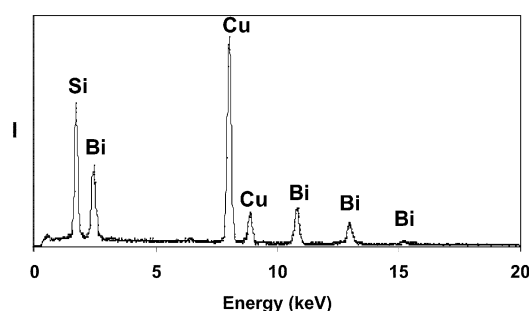
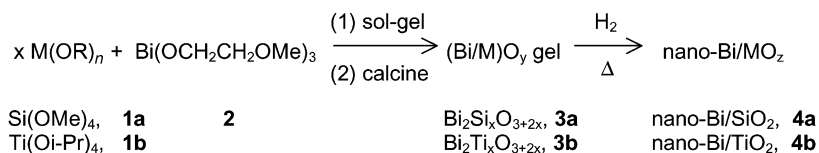


Fig. 1 EDS spectrum of nanocomposite **4a** (X-ray emission from the Cu grid of the sample holder is also observed).



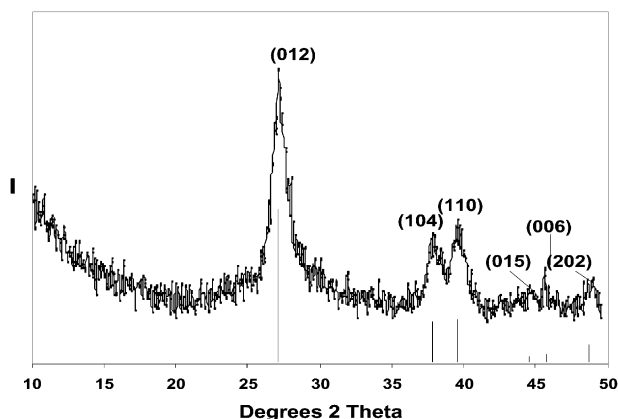


Fig. 2 XRD scan (Cu K $\alpha$  radiation) of nanocomposite **4b** along with the XRD line pattern of bulk Bi metal.

in Fig. 2. The most intense peak occurs at  $27.1^\circ$   $2\theta$  as is observed for Bi nanoclusters formed as near-surface species within silicate glass rods.<sup>4</sup> Analysis of XRD peak widths using Scherrer's equation gives volume-weighted average Bi particle diameters of 14.3 nm for nanocomposite **4a** and 6.3 nm for nanocomposite **4b**. Both nanocomposites apparently contain some fraction of Bi particles having diameters significantly larger than the number-average particle sizes determined by TEM. This observation might be expected for nanocomposites containing such high Bi loading due to local pooling of liquid Bi within the pores of the ceramic host matrix during thermal reduction. XRD scans from  $10$ – $50^\circ$  in  $2\theta$  of the intermediate Bi–Si mixed-metal oxide gel **3a** reveal only amorphous scattering and provide no evidence for the formation crystalline Bi<sub>2</sub>O<sub>3</sub>.

Addition of *ca.* 10 equiv.% Te(OEt)<sub>4</sub> to the sol–gel preparation **4a** gives a n-doped Bi–Te alloy/silica xerogel nanocomposite, **4c**. An EDS spectrum of this composite (Fig. 3) confirms the presence of Si, Bi, and Te with a Te doping level of *ca.* 5.5 wt%. XRD scans reveal a pattern of peaks consistent with the (012), (104), (110), (015), (006) and (202) peaks expected of a bulk Bi–Te alloy.<sup>11</sup> No peaks due to phase-separated Te are observed.

TEM micrographs of thin specimens of **4c** reveal Bi–Te nanocrystals of very high contrast and nearly regular hexagonal shape, as shown in Fig. 4. Careful etching of the silica matrix with aqueous HF solution leads to the isolation of these alloy nanocrystals free of the ceramic matrix. TEM micrographs of these isolated Bi–Te nanocrystals reveal some deterioration of nanoparticle shape. In addition, lattices fringes of 0.228 nm spacing are observed across the full diameter of the nanoparticles and are assigned to the (110) lattice planes of the expected rhombic unit cell. The corresponding *d*-spacing in elemental Bi is 0.2273 nm. XRD studies of Bi–Te alloys reveal a change in unit cell volume of only 0.45% upon enrichment of the Te content by 10 atom%.<sup>11</sup> Lattice fringes measured for

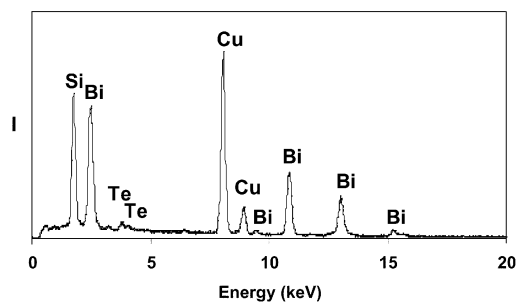


Fig. 3 EDS spectrum of nanocomposite **4c** (X-ray emission from the Cu grid of the sample holder is also observed).

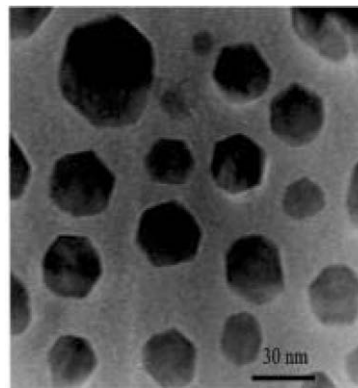


Fig. 4 TEM micrograph of nanocomposite **4c** (bar = 30 nm) showing Bi–Te alloy nanocrystals having hexagonal shape.



Fig. 5 Photograph of a pellet of nanocomposite **4b** formed by powder compaction in comparison to a U.S. dime coin.

nanocrystals of the Bi–Te alloy, **4c**, should, therefore, not differ significantly from the corresponding values known for elemental Bi. Single-domain nanocrystals are apparently produced by this synthesis method, although SAD patterns of isolated, single nanocrystals have not been obtained for nanocomposite **4c**.

Compaction of nanocomposite **4b** under 7000 lb pressure at room temperature produces a pellet 1.2 cm  $\times$  3 mm in size, as shown in Fig. 5. The pellet is sufficiently robust to survive stresses associated with normal manipulation.

The observations described above provide convincing evidence that Bi or Bi–Te alloy/ceramic nanocomposites of high metal loading can be conveniently prepared by selective *in situ* hydrogen reduction of Bi(III) and/or Te(IV) ions present within mixed-metal oxide gels. In addition, Bi/TiO<sub>2</sub> gel nanocomposites can be pelletized using moderate compaction conditions. Attempts to extend this synthetic strategy for the preparation of other nanostructured elemental Bi or Bi alloy/ceramic composites particularly those involving meso-structured ceramic host matrix materials are underway.

## Experimental

Reaction of the Bi(III) alkoxide, **2**, with pre-hydrolyzed TMOS (2.5 mL TMOS; 1 equiv. water; 0.2 mL 1.0 M aqueous NH<sub>3</sub> as catalyst) or with Ti(Oi-Pr)<sub>4</sub> **1b**, (1.0 mL **1b**; 10 equiv. water) in 2-methoxyethanol solution at room temperature gives a mixed-metal gel. The wet gels are harvested, washed with THF to remove solvent and alcoholic products, and dried in air at 125 °C. Calcination in air at 400 °C for 1 h affords the mixed-metal oxides, **3a** and **3b**, as dry powders. Reduction in a stream of hydrogen gas (flow rate of 150 mL min<sup>-1</sup>) with a tube furnace at 250 °C for 5 h gives the nano-Bi/metal oxide composites, **4a** and **4b**, as black powders of uniform color. To enhance the crystallinity of the Bi nanoclusters, the reduced composites are slowly cooled to room temperature over 10 hours under a N<sub>2</sub> atmosphere.<sup>6</sup> Elemental analysis of these nanocomposites (EDS and commercial microanalysis) reveals Bi loading of 35 and 47 wt%, respectively.

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