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Microengineered Conducting Composites from Nanochannel Templates**

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Metallic nanostructures can be prepared from nanochannel dielectric hosts by injection of the conducting melt. Nanowire arrays and random networks have been fabricated in this way. The role of the microstructure in the bulk electronic properties of the composites as well as applications of these materials are discussed.

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1. Introduction

Recent advances in nanotechnology, such as novel synthesis and processing methods and scanning microscopies, have opened up research opportunities on materials with ultrafine microstructures.¹ In particular, the design of composite materials consisting of a mixture of conducting and insulating phases in the nanometer range has flourished in the last few years. The bulk electronic properties of such nanocomposite may be tailored by altering the constituents, their size and shape distributions, or their relative concentrations. For example, semiconductor- and metal-insulator nanostructures exhibit a modified optical response as a result of size, shape, and surface effects and have applications to selective optical filters, transparent electrical contacts, and nonlinear optical elements.

2. Nanocomposite Synthesis

Natural and man-made or artificial dielectrics with an accessible microporosity can be utilized as host or template for the synthesis of nanocomposites by inserting a conducting phase into the pores. The composite microstructure is then determined by the pore structure of the host. The template strategy has been employed to chemically synthesize semiconductor and metal nanoparticles in microporous dielectrics²⁻⁴ and in the cavities of zeolites.⁵ In those cases the conducting phase occupies a volume fraction typically less than a few percent. Many practical applications, such as those involving electrical transport, require a high concentration and a connectivity of the conducting phase. We focus here on dense nanocomposites, i.e., those in which the active phase occupies a volume fraction of several tens percent.

2.1 High Pressure Injection

We have prepared dense nanocomposites by high pressure injection of the conducting

melt into nanochannel insulating templates.^{6,7} An externally applied hydrostatic pressure is needed to overcome surface tension effects which prevent the melt from entering the narrow channels of insulating hosts. The magnitude of such pressure depends on the surface tension of the melt and its wetting properties, and it is inversely proportional to the channel diameter. For a channel diameter of 10 nm, the required injection pressure ranges between 0.5 and 3.5 kbar for most metals and semiconductors. Details of the composite preparation process have been described elsewhere.⁷

The injection technique produces dense nanocomposites and insures the interconnectivity of the conducting phase. It also presents advantages over chemical preparation routes with respect to the composition and chemical purity of the composite. The range of composites which can be prepared by injection is limited by the sintering of the template which takes place at elevated temperatures. The sintering of the nanochannel insulators discussed in the following sections sets an upper limit on the melting temperature of the impregnant of about 1400 °C.

3. Composite Microstructure

The electronic properties of the nanocomposites are strongly dependent upon the topology and connectivity of the microstructure. In this context, man-made or artificial templates of controllable porosity (geometry, size, volume fraction) offer clear advantages over other templates such as natural zeolites and minerals. In continuation we discuss two distinct types of composites, with random and regular microstructures, synthesized from artificial ceramic templates.

3.1 Nanoscale Networks

We have prepared and examined nanocomposites where the conducting phase is in the

form of a network of strands as small as 6 nm in diameter.⁸⁻¹⁰ Commercial silica glasses which support an interconnected network of channels of average pore diameter ranging from 5.6 nm to 300 nm and 30% to 60% porosity were used as template.¹¹ Figure 1 shows a scanning electron microscope (SEM) photograph of a porous silica, the 5.6 nm average channel diameter is too small to be resolved by the SEM. The properties of the composites are highly reproducible since the impregnant "copies", to a large extent, the channel structure of the matrix. The three-dimensional conducting networks thus formed consist of small, randomly oriented crystallites. Since the material is homogeneous on the length scale of optical wavelengths, elastic light scattering is minimized and the metallic and semiconducting networks can be applied to the design of optical filters and selective absorbers. The electrical and thermal properties of the nanocrystalline networks may find applications to improved thermoelectric composites for efficient cooling and power generation.

3.2 Nanowire Arrays

The use of regular nanochannel templates allows for the preparation of nanocomposites where physical properties are easier to interpret and more amenable to theoretical treatments. Polycarbonates with pores made by nuclear track etching have been used to fabricate one-dimensional metallic structures by electrochemical deposition.¹²⁻¹³ We have employed nanochannel alumina to prepare high density arrays of metallic wires by injection of the melt.¹⁴ The commercial alumina has about 50 % porosity in the form of parallel, cylindrical channels.¹⁵ A micrograph of the nanowire array is shown in Figure 2.

In some cases, the nanowires can be made with a preferred crystallographic orientation relative to their length. This is illustrated in Figure 3 by the x-ray diffraction spectra from trigonal tellurium and bismuth telluride nanowire arrays. The spectra are dominated by

diffraction peaks from crystal planes parallel to the hexagonal c-axis and indicate that the crystal grains, of minimum size along the wire length of about 80 nm (from the diffraction peak widths), are oriented with the c-axis perpendicular to the wire length. Fundamental issues pertaining to crystal growth under microscopic geometrical constraints need to be examined in order to account for the oriented crystallite nanowires, such as the surface energies of different crystal faces with the confining walls.

Applications of the nanowire composites will tap their potential to create substantial electric field patterns over the sample surface. They include high density electrical multifeedthroughs and high spatial resolution charge transfer plates and photodetector arrays. A newly developed scanning force microscopy technique has allowed us to map with high spatial resolution the electric fields generated by the nanowires when charged.¹⁴

The nanowire arrays can also be microengineered to become optically transmissive and used as transparent electrical contacts. Good optical transparency and electrical conductivity can be simultaneously achieved in a metal microstructure where there is electrical isolation along the photon electric field (i.e., the photon and current-driving electric fields are perpendicular) and a self-screening charge can be developed at the surface of the metal particles by the light field.¹⁶ Figure 4 shows the mid-infrared optical absorption of an array of indium nanowires for light propagating along the wire length. The absorption of the nanowires in this region is two orders of magnitude smaller than that of bulk indium and qualitatively follows the spectral shape predicted by simple effective medium theories.

4. Summary and Future Prospects

Novel nanostructures of conducting materials generated by the template approach are becoming available through a variety of syntheses, processes, and hosts. We have described a

class of electronic composites prepared by injection of the conducting melt into nanochannel templates. The recent development of regular, ultrasmall channel artificial templates^{17,18} will allow for the design of a new type of ordered nanocomposites.

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FIGURE CAPTIONS

- Figure 1: Porous silica (Vycor Code 7930, Corning) of 5.6 nm channel diameter and 33% porosity. The silica appears as light clusters, the channels in dark.
- Figure 2: Array of 250 nm diameter metallic wires, the wire density is about $5 \times 10^8 \text{ cm}^{-2}$.
(a) top view. (b) cross-section.
- Figure 3: Theta-two theta scans from 200 nm wires of trigonal Te and Bi_2Te_3 showing preferential crystallite orientation (c-axis perpendicular to the wire length). Peaks are labeled by the plane Miller indices. The relative intensities for randomly oriented crystallites are indicated in parentheses. The diffraction geometry is shown in the insert.
- Figure 4: Absorption coefficient of an array of indium wires 200 nm in diameter and $8 \mu\text{m}$ long (metal volume fraction close to 50%) for unpolarized light propagating along the wire length. For comparison, the absorption coefficient of bulk indium in this spectral region is about $1.3 \times 10^6 \text{ cm}^{-1}$. The increasing absorption at small wavenumbers is from the alumina template.

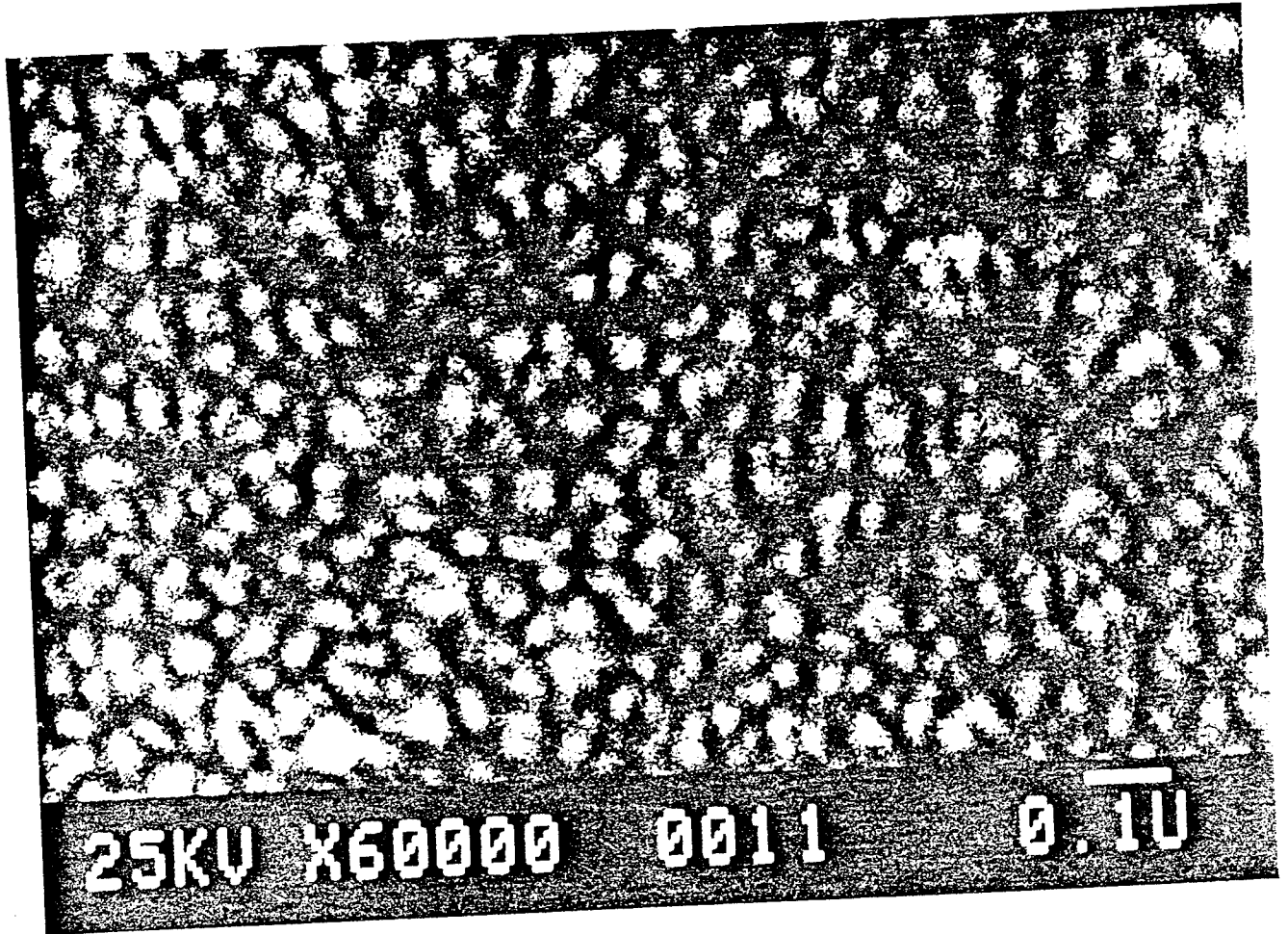


Figure 1

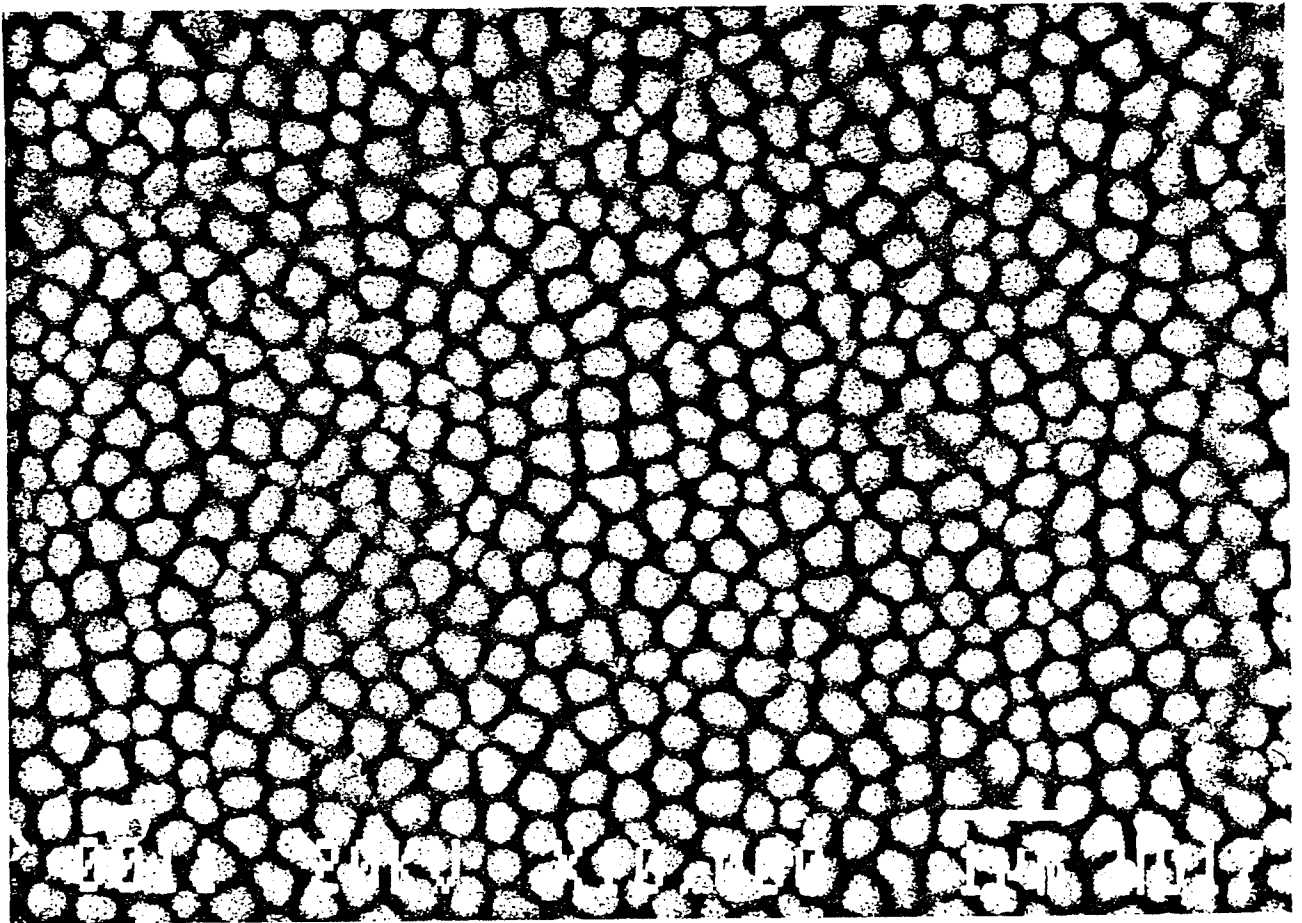


Figure 2.a

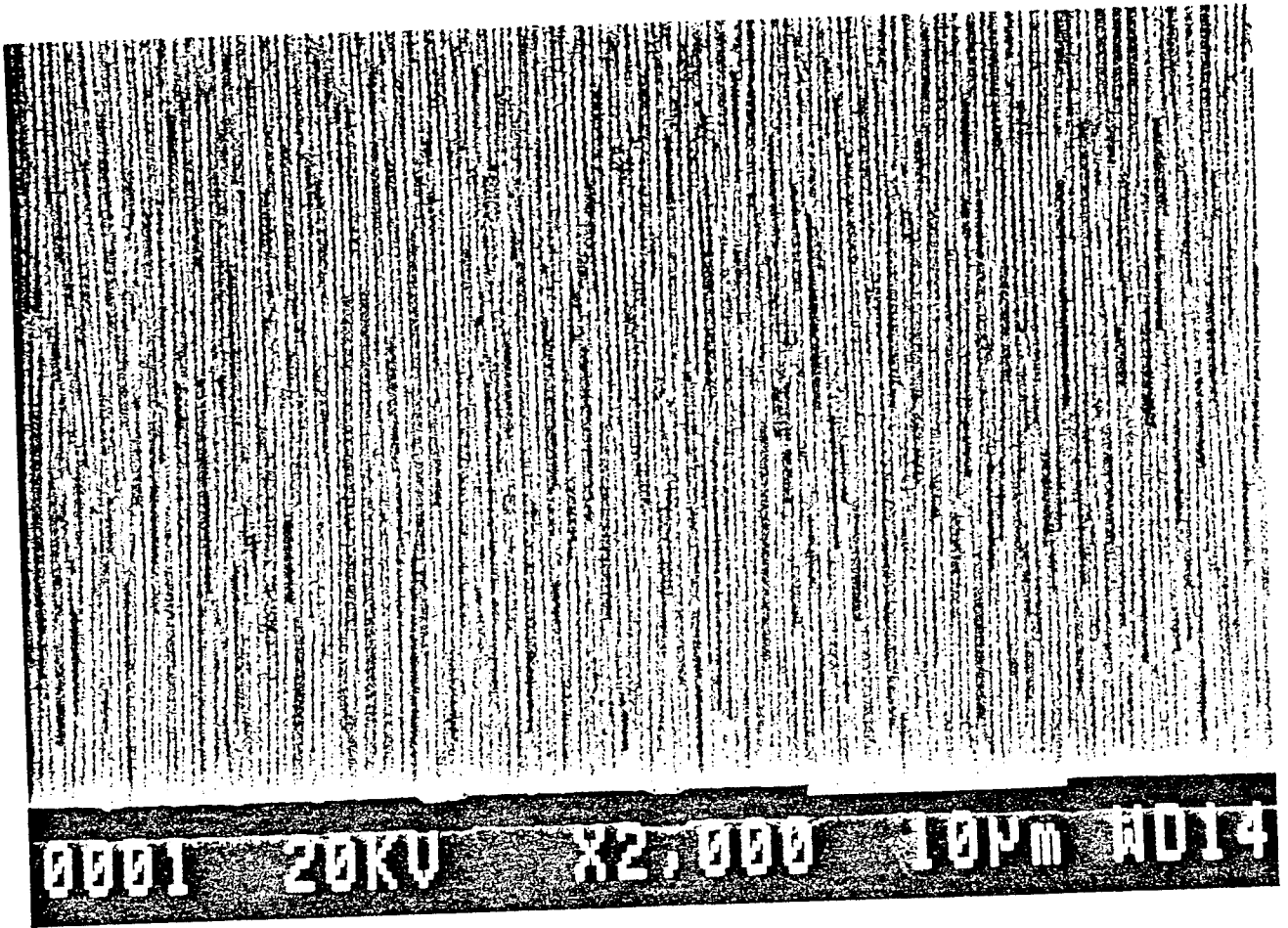


Figure 2.b

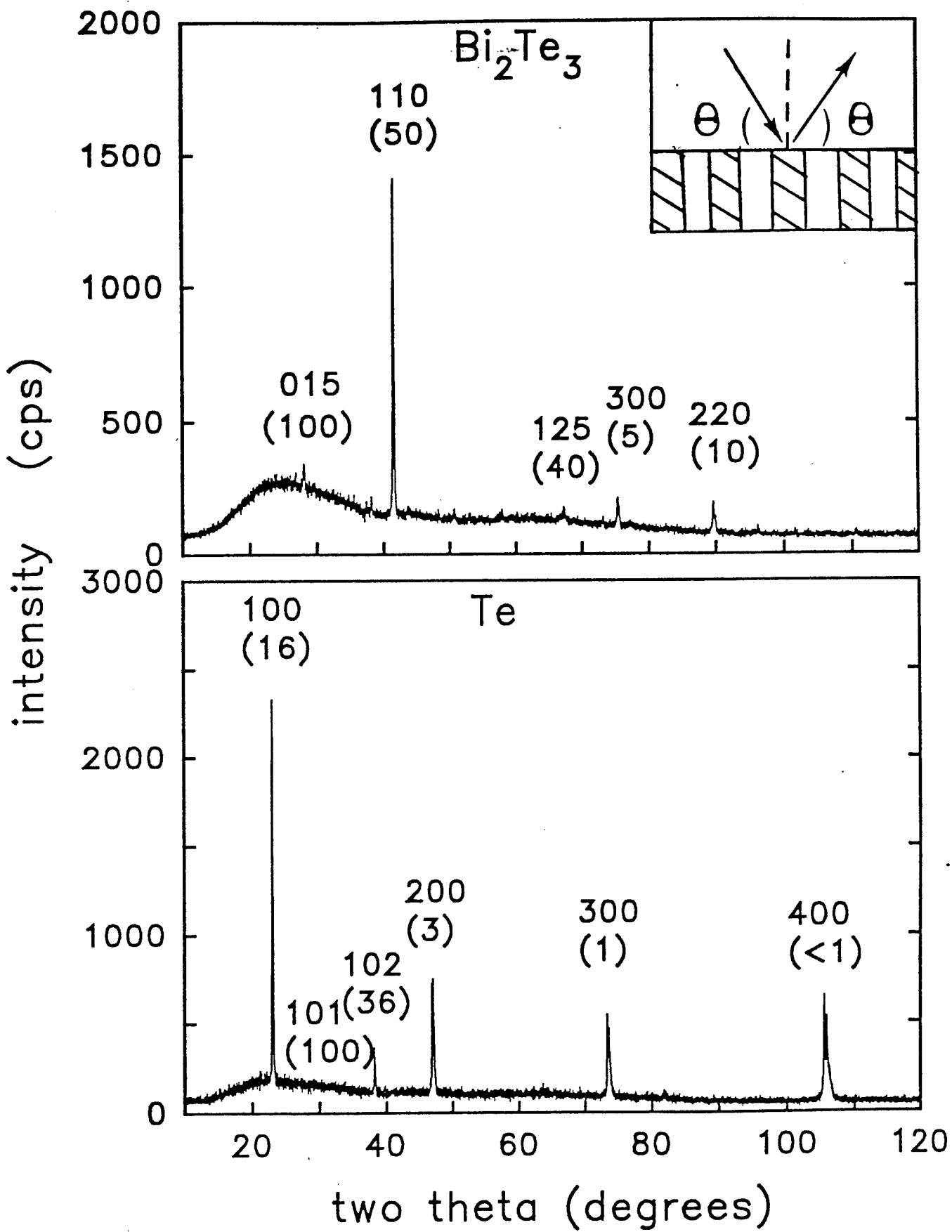


Figure 3

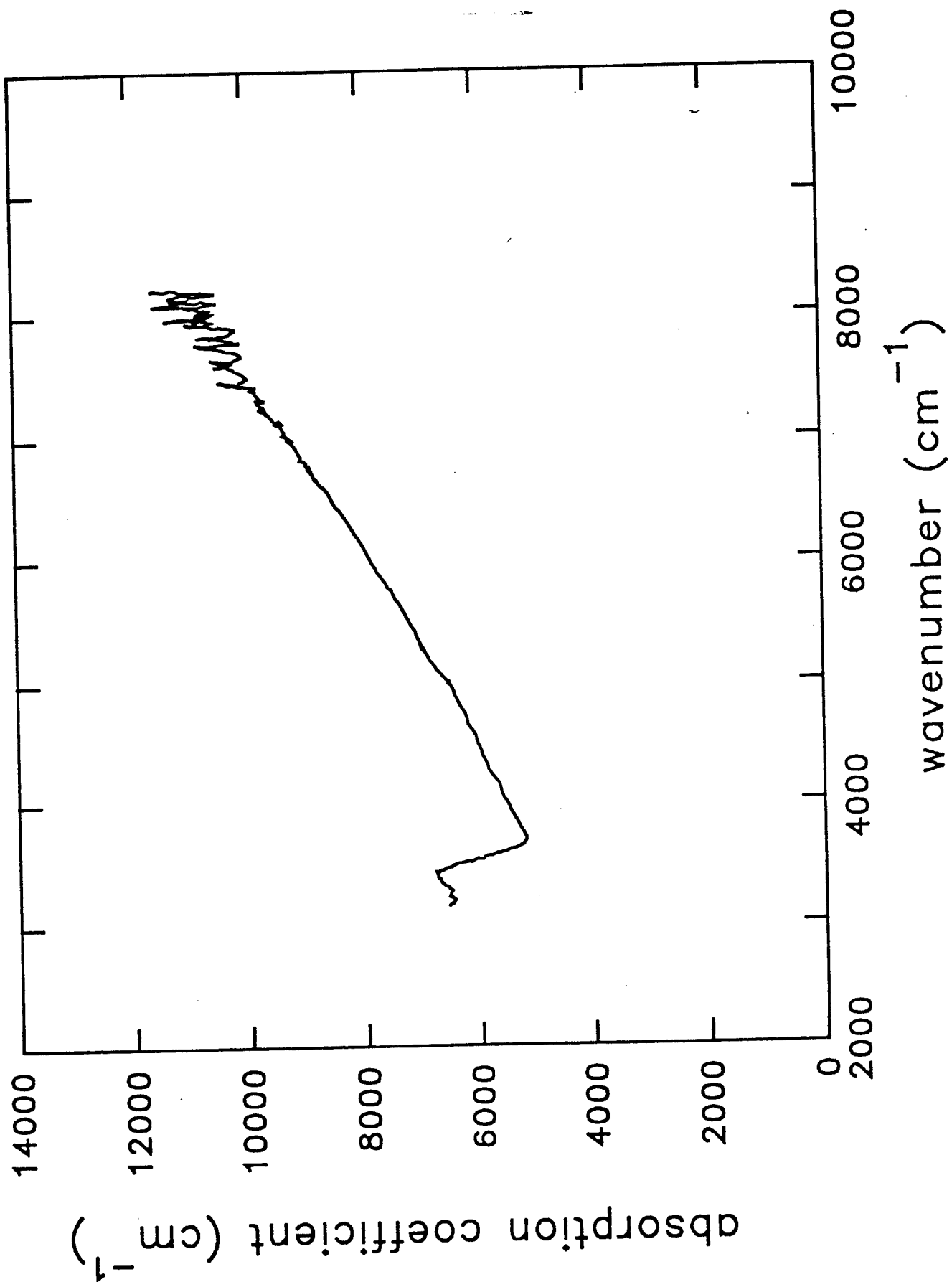


Figure 4