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Solar Energy Materials
& Solar Cells

Solar Energy Materials & Solar Cells 85 (2005) 477–488

www.elsevier.com/locate/solmat

Selective emitters for thermophotovoltaics: erbium-modified electrospun titania nanofibers

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Received 24 December 2003; received in revised form 26 April 2004

Available online 21 July 2004

Abstract

Titania nanofibers were synthesized by electrospinning and characterized with scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The nanofibers were annealed to 773 K to achieve the anatase titania crystal structure, and to 1173 K to obtain the rutile phase. In order to create erbium-containing titania nanofibers, erbium (III) oxide particles were added to the pre-cursor solution before electrospinning. After pyrolysis the titania nanofibers supported and encapsulated the erbium particles. Temperature-dependent near-infrared emission spectra demonstrate that the erbium-containing nanofibers emit selectively in the range 6000–7000 cm⁻¹. Because of their large surface to volume ratios and narrow-band optical emission, these nanofibers can be used as selective emitters for thermophotovoltaic applications.

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Keywords: Thermophotovoltaics; Selective emitters; Nanofibers; Electrospinning; Titania; Erbium

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1. Introduction

Thermophotovoltaic (TPV) effects provide the basis for a promising energy conversion technology for the production of electricity from the infrared (IR) light radiated by a heated emitter [1–10]. An idealized TPV system is comprised of a source of thermal energy which heats the emitter and an IR photovoltaic (PV) cell which absorbs the light and produces electricity. The thermal energy source is unrestricted and TPV systems create no noise or pollution. This technology is ideally suited for power generation in space and is a viable candidate for co-generation schemes in other situations. Emitters should be isothermal and produce light that can be efficiently absorbed by the PV cells. The spectral distribution of light from the emitters plays a key role in enabling this technology.

The approach described in this paper is based on the use of titania nanofibers with spectral emission tuned to the bandgap of GaSb photovoltaic cells. Tuning is achieved by incorporating erbia particles directly into electrospun nanofiber mats. We choose these “selective emitters” over blackbody-like (greybody) emitters, since greybodies emit much of their light in undesirable regions of the spectrum for efficient energy conversion by the PV cells. This requires greybody TPV systems to rely on optical filters placed between the emitter and collector to block the low- and high-wavelength light which would not produce electrical power. Filters and other schemes for energy recuperation add more components and types of materials to the TPV design, making the system more complex, harder to manufacture, and more difficult to maintain. We are investigating a simpler approach based on nanofiber selective emitters that does not require optical filters.

The major benefit of nanofibers over standard mantle designs is that a nanofiber selective emitter is in a form where the surface area (responsible for net light emission to the PV cells) is maximized while the volume (responsible for re-absorption of light and thereby preventing it from reaching the PV cells) is minimized. Cooler regions of the selective emitter will reabsorb the light from other parts of the structure and must be avoided. This is accomplished with nanofibers having large surface:volume ratios. In addition, nanofiber structures allow gases to pass through them with lower pressure drop than materials made from micron-sized fibers, and have increased mechanical stability due to larger length:diameter ratios. Here we describe the synthesis and characterization of potential nanofiber TPV emitters.

In this paper, long titania nanofibers and those modified with erbium oxide are fabricated by electrospinning followed by thermal pyrolysis. Erbium is a candidate selective emitter for GaSb cells. Titania is transparent in the near-IR regions where erbium emits, and is also thermally stable at the temperatures of interest here. The goal of this work is to demonstrate the synthesis and characterization of high-temperature nanofiber materials with optical properties tailored for TPV applications. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) data characterizing the structure and stoichiometry of the titania nanofibers are presented. The selective near-IR emission of heated erbium-doped titania nanofibers and future directions for using these in actual TPV applications are discussed.

2. Synthesis by electrospinning

While attention was paid to the types of structures and materials that can be produced at the nanoscale, nanotechnology is still in need of industrially relevant processes for synthesizing structures on a large scale. One process that has already scaled-up for manufacturing is electrospinning of polymer nanofibers. Electrospun nanofibers have potential uses as biomaterials, sensors, filtration media, and as we will show here, TPV emitters. Recently the electrospinning process has been used to produce hybridized polymer, ceramic, and metal oxide nanofibers, tubes, and supports for other particles and coatings [11–16].

In electrospinning, a polymer precursor solution is suspended in a pipette above a collector plate with a large voltage applied between the two. The drop that forms at the tip of the pipette becomes a cone, and a charged jet of the solution emerges when the forces due to electric fields overcome the surface tension of the drop. The jet elongates and follows a spiraling path caused by what is best described as an electrically driven bending instability. The properties of the resulting nanofibers depend on the precursor solution, the magnitude of the voltage, and the geometrical relationship between the pipette and the collector plate.

For the fibers discussed here, tetraisopropyl titanate (TPT) (TYZOR[®] TPT, from Dupont) was mixed with a 10% solution of polyvinylpyrrolidone (PVP) (average MW 360,000 from PolySciences, Inc.) in absolute ethanol. The mixture ratio of TPT to the PVP solution was varied from 0.008 to 1.38 by weight in order to optimize the process for nanofiber production. The mixtures were placed in a vertical pipette and electrospun using an electric field of 1 kV/cm. Metal flat washers or aluminum foils were used as the collectors during spinning. The fibers were hydrolyzed in air for 12 h and then heated in air to pyrolyze the PVP. For erbium-doped titania nanofibers, a 0.4 TPT:PVP weight ratio was used with erbium (III) oxide particles (Strem Chemical, Inc.) added to the solution before electrospinning. Fibers made using an erbium:TPT ratio of 1.0 by weight were produced and used in the following experiments.

3. Materials characterization

3.1. SEM and XRD of titania fibers

Scanning electron microscope images (JEOL JEM-5310) of titania fibers after pyrolysis are shown in Fig. 1 for three TPT:PVP precursor weight ratios. This ratio plays an important role in determining the diameters of the resulting fibers. At a very low (0.008) TPT:PVP ratio, continuous titania fibers cannot be produced by electrospinning. Increasing the TPT:PVP ratio to 0.02, irregular titania fibers with diameters less than 100 nm are formed as shown in Fig. 1A. This is the critical ratio for forming titania nanofibers that can survive pyrolysis under the conditions used in this work. Increasing the TPT:PVP weight ratio leads to an increase in the diameter and structural homogeneity of the titania nanofibers as seen in Fig. 1B for a 0.8

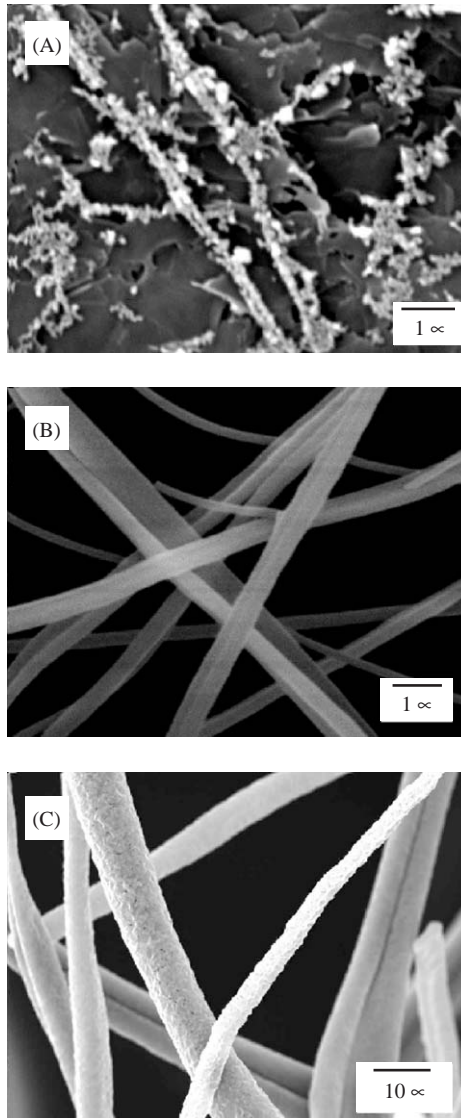


Fig. 1. Scanning electron microscope images of self-supporting and continuous titania fibers after pyrolysis. These structures result from electrospinning TPT:PVP solutions with ratios of (A) 0.02, (B) 0.8, and (C) 1.38 by weight. The scale bars in (A) and (B) are 1 μm , and in (C) the scale bar is 10 μm . A TPT:PVP weight ratio of 0.4 was found to be optimum and was used to produce the nanofibers discussed in the remainder of this paper.

weight ratio. Increasing the TPT content leads to fibers with diameters in the micron range, as shown in Fig. 1C for a 1.38 TPT:PVP weight ratio. For producing rare-earth doped nanofibers for selective emitters with large aspect ratios, a TPT:PVP ratio of 0.4 is chosen.

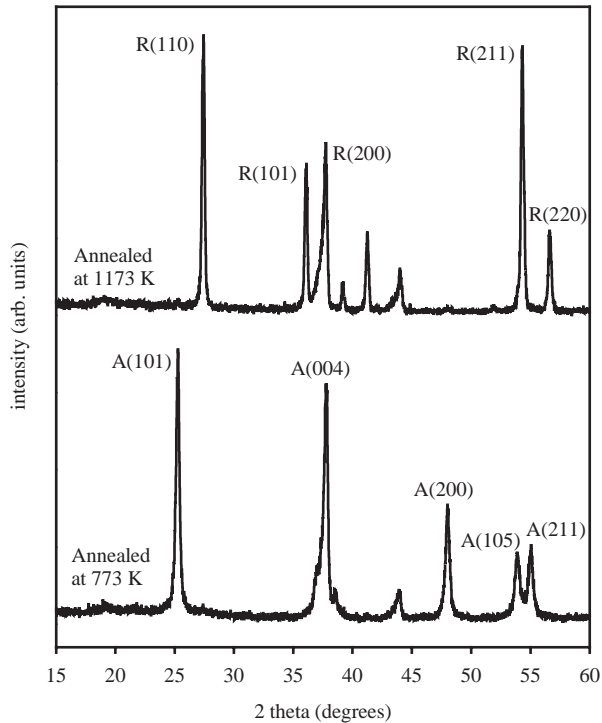


Fig. 2. X-ray diffraction patterns from titania nanofibers after 773 and 1173 K pyrolysis. The major assigned features in the lower pattern correspond to the anatase form of titania, whereas those in the upper pattern correspond to the rutile form of titania. Rutile is the thermodynamically stable form of titania nanofibers desired for TPV applications.

Titania has brookite, anatase and rutile crystal structures. Titania nanofibers were ground into powders and XRD (Philips PW 1710) measurements were performed. As shown in Fig. 2, the resulting diffraction patterns are strong. Annealing at 773 K in a sintering furnace pyrolyzes the PVP leaving anatase-phase titania nanofibers as indicated by the lower diffraction pattern of Fig. 2. Increasing the annealing temperature to 1173 K produced rutile-phase titania nanofibers as indicated by the upper diffraction pattern of Fig. 2. For TPV applications, the data of Fig. 2 indicate that titania nanofibers must be annealed at high temperature in order to achieve the desired thermodynamically stable rutile crystal structure. The major diffraction peaks are labeled in Fig. 2 using the notation $A(hkl)$ and $R(hkl)$, where A and R , respectively, stand for anatase and rutile, and the integers h , k , and l are Miller indices.

3.2. SEM and XPS of erbia-doped titania nanofibers

As shown in the SEM images of pyrolyzed erbia-doped titania nanofibers in Fig. 3, the fibers both support larger erbia particles (Fig. 3A), and encapsulate

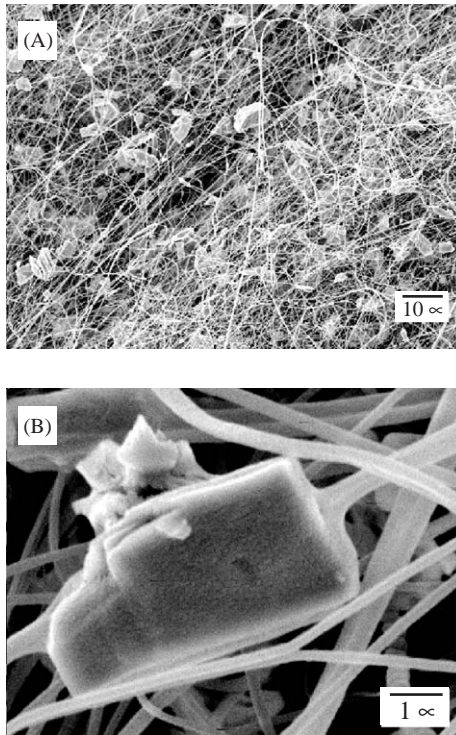


Fig. 3. Scanning electron microscope images of titania nanofibers doped with erbium particles. In (A), larger erbium particles are supported by the nanofiber mesh. The scale bar in (A) is 10 μm . Panel (B) shows that smaller erbium particles are encapsulated within titania nanofibers. The scale bar in (B) is 1 μm .

smaller erbium particles (Fig. 3B). This provides significant flexibility in our selective emitter development. In Fig. 3A the titania nanofibers have very large length:diameter ratios and form a random non-woven mat with many pores for gas to flow through. Both qualities are useful for TPV systems. Fig. 3B demonstrates the encapsulation of erbium particles which should lead to excellent thermal equilibration, also desirable for selective emitter development.

X-ray photoelectron spectroscopy (Kratos ES 300) measurements characterize the chemical composition of our titania nanofibers. Survey scans of pyrolyzed titania nanofibers and of those incorporating erbium particles are presented in Fig. 4. These spectra have been vertically separated for clarity but no background fitting has been performed. As expected, all the fibers contain Ti, O, and C, and the upper spectrum in Fig. 4 shows the presence of erbium as well. The low intensity of the Er feature is due to the small amount of erbium present at the surface of these nanofibers and to the low photoelectron cross section of Er. Higher resolution scans were also collected, and after smoothing and background fitting the spectral features were integrated and corrected for atomic sensitivity factors of the spectrometer. This yielded the following percent compositions for the erbium-doped nanofibers: O (44%),

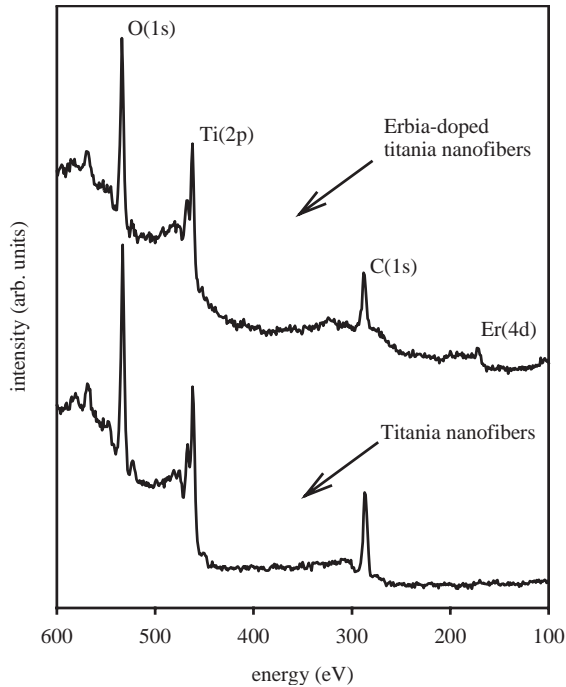


Fig. 4. X-ray photoelectron survey scans of pyrolyzed titania nanofibers and of those incorporating erbia particles. Carbon retained after pyrolysis could not be removed by ion sputtering without damaging the nanofibers. The intensity of Er(4d) photoelectron emission is low because there is only a small percentage of the erbium exposed at the surface of the fiber mat and because the erbium photoelectron ejection process has a low probability.

C (39%), Ti (15%) and Er (2%). Attempts to remove the adventitious carbon and to do depth profiling with Ar ion sputtering damaged the nanofibers.

4. Infrared emission characterization and discussion

4.1. Nanofibers supported on a greybody heater cartridge

The optical properties of the nanofibers were studied using a Nicolet Fourier transform infrared bench (Nexus 670). The near-IR absorption spectra of titania nanofibers are essentially featureless since they are transparent, whereas erbia powder has strong absorption features (not shown). Our data indicate that the absorption features of erbia-doped nanofibers after pyrolysis are essentially identical to those of erbia powder, which is not surprising. Emission spectra were then collected using the optics from a Raman system, which directed the IR light emitted by the hot nanofibers into the FTIR optical system. The nanofibers were electrospun directly onto a 200 W cylindrical steel cartridge heater about 1 cm in diameter and

5 cm long. The temperature of the heater was controlled with a variable transformer and calibrated with a thermocouple spot-welded directly to the cartridge surface. The temperature was stable to within 5 K. The nanofibers were heat-treated for conversion to the rutile form before the emission measurements.

Fig. 5 presents raw IR emission spectra from erbia-doped titania nanofibers supported by the cartridge heater at several different temperatures. Note that these are lower temperatures than the usual TPV design operating temperatures (> 1200 K). Although the signatures of erbia are present, greybody emissions from the heater dominate the spectra. This spectral “shine-through” is the reason that selective emitter coatings are ineffective at significantly advancing TPV technology. Emitted spectra such as these still require optical filtering for TPV. Fig. 6 presents the same spectra as in Fig. 5, but with background spectra subtracted. The background spectra are measured at the temperatures indicated using a heater cartridge painted with carbon paint. The subtraction is performed to avoid any artificial negative intensity values. The vertical scales of Figs. 5 and 6 are in the same arbitrary units for comparison. Note that the greybody contribution is still present even after background subtraction, but that selective emission from the erbia-doped nanofibers is evident.

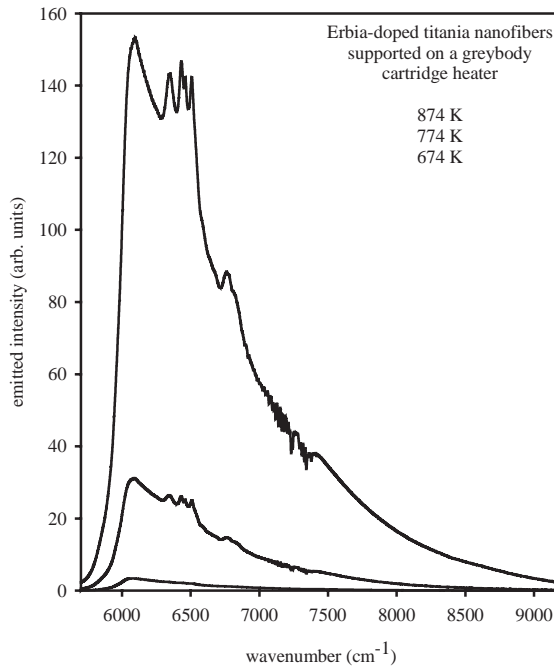


Fig. 5. Raw near-IR emission spectra from erbia-doped titania nanofibers at several different temperatures. The nanofibers were electrospun directly onto the surface of a metal cartridge heater. Note that the greybody spectral shine-through from the heater dominates. The spectra are vertically stacked based on temperature: lower = 674 K, middle = 774 K, upper = 874 K.

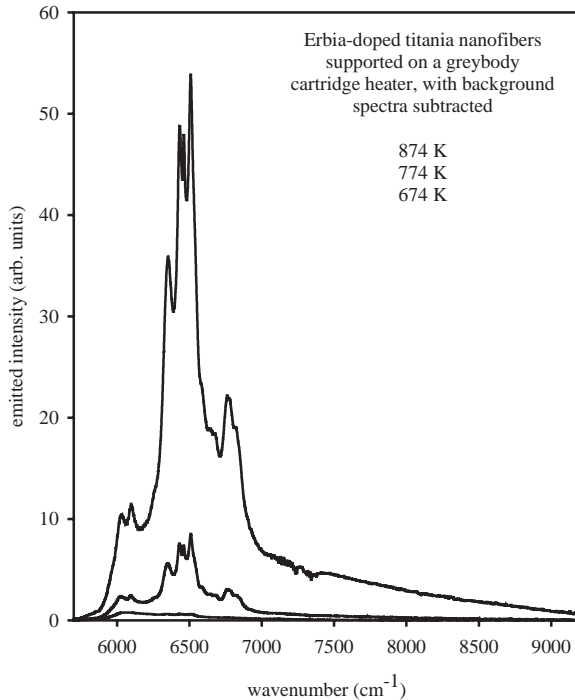


Fig. 6. Emission spectra from the same data set as in Fig. 5, but with background spectra subtracted. The background spectra are measured with a cartridge heater painted with carbon paint. The subtraction is performed to avoid any negative intensity values. The spectra are vertically stacked based on temperature: lower = 674 K, middle = 774 K, upper = 874 K.

4.2. Self-supporting nanofibers in a convectively heated quartz tube

Dispersing erbia in a self-supporting nanofiber mat will significantly improve the selective emission process by increasing the surface:volume ratio and approaching isothermal conditions. This should allow TPV systems to operate at temperatures such as those found in waste exhaust streams. To test this hypothesis, pyrolyzed nanofibers are placed in an open cylindrical quartz tube about 1 cm in diameter and 25 cm long in the form of a “lazy L”. The geometry of the setup with respect to the FTIR optical system is the same as for the heater cartridge. Nanofiber mats (a few milligrams of material that look to the eye like pieces of facial tissue) are placed in the vertical section of the tube. Convective heating of the nanofibers is accomplished by the hot off-gases from a propane torch aimed at the lower opening of the tube. The “lazy L” design is an attempt to avoid a direct line of sight between the hot torch and the collection optics. Estimates of the nanofiber temperature are made with a small type-K thermocouple inserted through a small hole in the wall of the tube and fixed with high-temperature cement. The temperature stability is good to about 5 K.

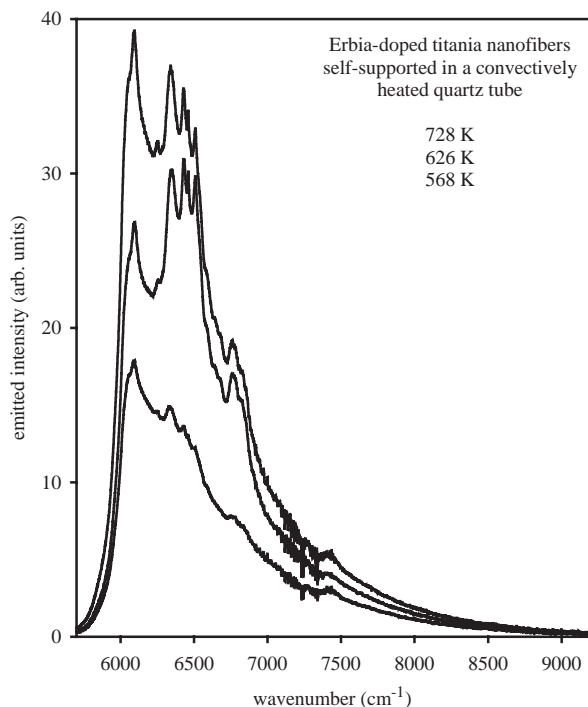


Fig. 7. Raw near-IR emission spectra from erbium-doped titania nanofibers at several different temperatures. The fibers are in the form of a self-supporting mat located in a vertical quartz tube and heated convectively by hot gases from a remote propane flame. The temperature of the region containing the fibers is measured with a thermocouple. The spectra are vertically stacked based on temperature: lower = 568 K, middle = 626 K, upper = 728 K.

We present raw IR emission spectra from erbium-doped titania nanofibers in Fig. 7. The spectra are from erbium-doped nanofibers while they are at the temperatures shown in the inset. Note that these are lower temperatures than standard TPV design operating temperatures (> 1200 K). As in Fig. 5, there is some greybody contribution to the spectra. However, in the case of the self-supporting nanofibers of Fig. 7 the erbium emission is more significant than the background. Fig. 8 presents the same spectra as in Fig. 7, but with measured background spectra subtracted. The background data are measured using the empty quartz tube at the temperatures indicated (within 5 K). The propane torch heats the bench optics and surroundings that in turn produce a greybody signature. The subtraction is scaled to avoid any artificial negative intensity values. The vertical axes of Figs. 7 and 8 are in the same arbitrary units as those of Figs. 5 and 6.

The spectral matching provided by selective emitters produces light that the PV cells can efficiently convert to electricity and minimizes the necessity for other spectral control measures. Designs based on nanofibers promise significant advances in thermophotovoltaic technology. The rate of thermal energy conduction in the

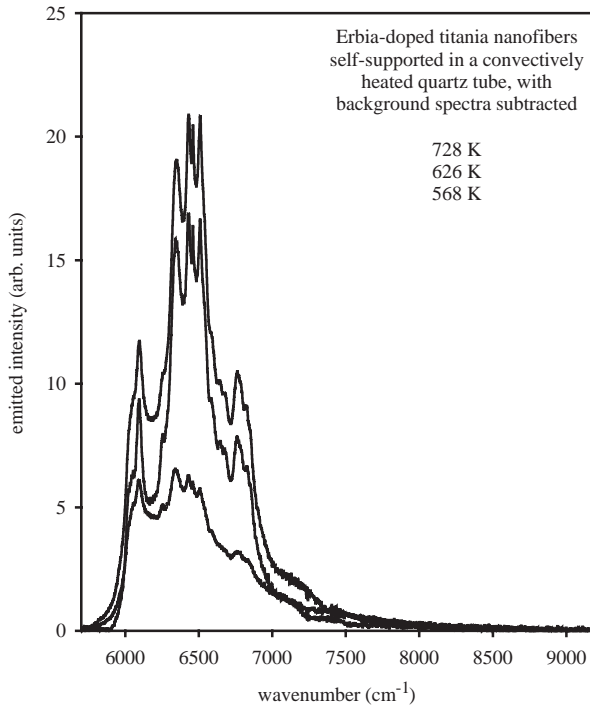


Fig. 8. Emission spectra from the same data set as in Fig. 7, but with background spectra subtracted. The background spectra are measured with an empty quartz tube at the temperatures indicated and result from the greybody signature of the optics and surroundings that are heated by the propane torch. The subtraction is performed to avoid any negative intensity values. The spectra are vertically stacked based on temperature: lower = 568 K, middle = 626 K, upper = 728 K.

radial direction in a fiber of diameter (d) depends on d^{-1} , and a nanofiber is essentially an isothermal surface with very little volume (surface:volume ratio also depends on d^{-1}). This means that the thermal time constant of a nanofiber is reduced as the volume becomes small. Finally, mantle structures presently made from large fibers of oxide materials are mechanically fragile. Nanofibers having large length:diameter ratios can flex to alleviate mechanical stresses.

5. Summary

In this work, titania nanofibers were synthesized by electrospinning and subsequent annealing, and then characterized by SEM, XRD, XPS and FTIR. We demonstrated that we can control the diameters of the nanofibers by adjusting the pre-cursor solution, and that we can alter their crystal structure by annealing to different temperatures. Erbium-containing titania nanofibers were also produced and characterized, and it was shown that the titania nanofibers supported and

encapsulated the erbia particles. Temperature-dependent near-infrared emission spectra show that the erbia-containing nanofibers emit selectively in 6000–7000 cm^{-1} range. Selective emission performance was optimized with self-supporting nanofiber mats, which were tested under conditions similar to those in hot waste streams and exhaust systems. The large surface to volume ratio, good thermal stability, and narrow-band emission properties of these nanofibers make them candidate selective emitter materials for thermophotovoltaic applications. The data presented here indicate that nanofiber electrospinning provides a new approach to enabling TPV systems that use selective emitter materials.

Acknowledgements

The authors would like to thank The University of Akron, DOE NETL, and the National Science Foundation (DMII 0100354) for support of this project. We are also grateful to Professor J.R. Elliott, Jr., for the use of his near-IR spectrometer, and to Mr. Tom Quick for acquiring the X-ray diffraction data.

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