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Synthesis and characterization of erbia doped metal oxide nanofibers for applications in thermophotovoltaics

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Titania (TiO₂) nanofibers doped with erbia (Er₂O₃) have been synthesized by electrospinning mixtures of polymers, titanium-containing materials, and erbia particles. These electrospun nanofibers are subsequently annealed at temperatures of 800, 900, 1000, and 1050 °C to remove the organics and leave behind the metal oxides. The crystal structure and optical properties of the metal oxides depend on the annealing temperature, and we characterize these nanofibers using x-ray diffraction and Fourier transform infrared spectroscopy (FTIR). An Er₂Ti₂O₇ phase is formed in an amount which depends on the annealing temperature, and relationships between the nature of FTIR spectra and the relative amounts of different phases are demonstrated. Finally, the relevance of this work to thermophotovoltaics and other applications is discussed. © 2007 American Vacuum Society. [DOI: 10.1116/1.2742390]

I. INTRODUCTION

It has been shown in the past that the elemental and chemical composition and the morphology of electrospun nanofibers are very sensitive to the synthesis conditions. The effects of solution chemistry and electrospinning procedure have been investigated in some detail, and a recent review¹ summarizes much of this work on nanofibers. In our own labs we have seen a variety of unexpected behavior which further demonstrates the strong influence of electrospinning conditions on the resulting nanofibers. For example, in a recent study on electrospun titania nanofibers, we found that silicon can be unintentionally introduced into the nanofibers as a result of the solution being in contact with silicone tubing used in the electrospinning apparatus.² Additionally, in a recent letter, we demonstrated that carbon dioxide can remain in metal oxide nanofibers as a side effect of the annealing process.³

One of our continuing efforts is to develop metal oxide nanofibers doped with rare earth ions for applications in thermophotovoltaics (TPV).⁴⁻⁷ Specifically, we are interested in low temperature (<1000 °C) applications. This is an appropriate temperature range for TPV systems designed specifically to recover some of the wasted thermal energy from exhaust streams; automobiles would be a common example.

The metal oxide nanofibers described in this paper are formed by a two step process which involves the electrospinning of composite polymer/metal precursor nanofibers and subsequent annealing to remove the polymer and control the crystal structure. Further investigation of the effect of annealing conditions on the chemical and physical nature of

erbia doped electrospun metal oxide nanofibers is described in this study as a natural extension of our previous work.

Our main interest is in tracking changes in the near-IR signature bands of Er³⁺ centered approximately at 6500 and 10 300 cm⁻¹. These IR features result from forbidden intra-band 4*f* electronic transitions. Specifically, the transitions from the ⁴I_{15/2} state to either the ⁴I_{13/2} or ⁴I_{11/2} states, respectively, lead to these two near-IR bands.⁸ The physical mechanisms behind this type of electronic transition in rare earth ions has been investigated theoretically in detail by Smentek.⁹ In addition to spin-orbit coupling, electron correlation effects were shown to be important, while the crystal field from the matrix surrounding the rare earth ion was treated as a perturbation. A more recent investigation involving both theory and experiment by Torsello *et al.* provides a comprehensive explanation of the selective emission process from materials containing rare earth ions.¹⁰ It was shown that the crystal field symmetry has a large effect on the efficiency of nonradiative decay channels. These nonradiative pathways compete with the desired radiative decay channel and reduce the emissivity. The two studies by Smentek⁹ and Torsello *et al.*¹⁰ demonstrate that although the 4*f* levels of Er³⁺ are shielded by the 5*p* and 5*s* electrons, they are still perturbed by the local crystal field and we therefore expect to see changes in the near-IR spectra when the local environment of the Er³⁺ changes.

The IR features of Er³⁺ are of interest because some materials which contain these species can be used as selective emitters for TPV applications.^{4,5,7,10} The spectral feature around 6500 cm⁻¹ is relevant for TPV applications which incorporate low band gap photocells (e.g., InGaAs or GaSb).⁸ The spectral feature around 10 300 cm⁻¹ is of less

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significance in these applications, but nevertheless it is interesting to study these spectral features as well from a scientific point of view.

$\text{Er}_2\text{Ti}_2\text{O}_7$ has a pyrochlore crystal structure that has been studied by other groups because of its interesting optical¹¹ and magnetic¹² properties. It has been abbreviated as both “ETO” and “ErT,” and in this paper we use the ETO abbreviation.

II. EXPERIMENT

A. Materials and synthesis

Nanofibers were made using the electrospinning technique with a system that is similar to those described elsewhere.¹³ Solutions containing polymer, solvent, and metal precursor materials were spun at an initial syringe pump rate of 35 $\mu\text{L}/\text{min}$ for 10 min and then 15 $\mu\text{L}/\text{min}$ thereafter. The acceleration voltage was approximately 20 kV and the distance between the electrospinning tip and the aluminum foil collector which spun at 50 revolutions per minute was about 20 cm.

The solution used was prepared by first mixing 3 g of polyvinylpyrrolidone powder (PVP, Sigma-Aldrich, Mwt: 1,300,000, CAS 9003-39-8) with 50 g of absolute ethanol. This PVP solution was then mixed with 5.7 g of TYZOR® tetraisopropyl titanate (TPT, Dupont), chilled in ice for 3 h, then stored at room temperature for approximately one week before using.

Erbia particles were mixed in the PVP/TPT solution using a magnetic mixer for 2 h. The mixture was then mixed in an ultrasonic bath for about 10–15 min. The nanofibers were spun immediately following the ultrasonic mixing. After the nanofibers were removed from the aluminum foil collector, they were annealed in a tube furnace. The heating rate was 5 $^\circ\text{C}/\text{min}$, and the temperature was held at the reported annealing temperatures for 2 h. Finally, the furnace was allowed to cool to room temperature before the annealed nanofibers were removed.

B. Fourier transform infrared spectroscopy (FTIR)

FTIR measurements were performed with a Bruker IFS 66v/s using a Harrick “praying mantis” diffuse reflectance (DRIFTS) accessory. The experiments were all performed under vacuum (typically 3 mbars) with a resolution of 4 cm^{-1} . A tungsten source, CaF_2 beamsplitter, and thermoelectrically cooled InGaAs detector were used.

C. X-ray diffraction

X-ray diffraction patterns were collected with a Philips PW1710 based instrument using a copper anode normally operating at 40 kV and 35 mA. Samples were ground into a powder then mixed with acetone to make a paste that would adhere to a substrate. A sample spinner was not used. Peak assignments were performed using the ICDD pdf-2 database.¹⁴

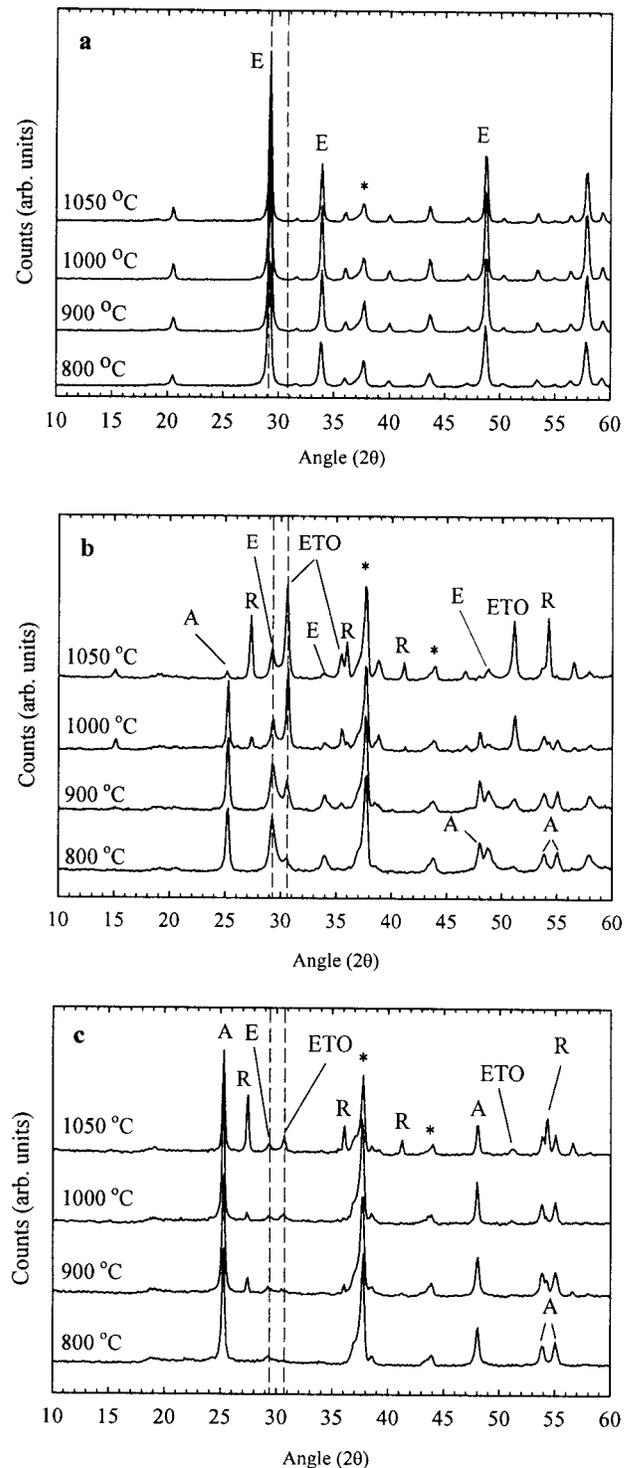


Fig. 1. XRD plots at four annealing temperatures for (a) erbia powder, (b) erbia doped titania nanofibers with a nominal atomic ratio of Er:Ti=0.54, and (c) erbia doped titania nanofibers with a nominal atomic ratio of Er:Ti=0.067. The labels are (E) erbia, (A) anatase titania, (R) rutile titania, (ETO) $\text{Er}_2\text{Ti}_2\text{O}_7$, and (*) instrumental artifacts. The vertical dashed lines are drawn for the main peaks of the erbia and $\text{Er}_2\text{Ti}_2\text{O}_7$ used for quantification (see text).

III. RESULTS AND DISCUSSION

The x-ray diffraction (XRD) plots in panel (a) of Fig. 1 show that annealing only the erbia particles at temperatures

of 800, 900, 1000, and 1050 °C does not significantly change their crystal structure. However, annealing the nanofibers doped with erbia in an atomic ratio of Er:Ti = 0.54 has a distinct influence, as shown in panel (b) of Fig. 1. The ETO phase becomes more apparent in the XRD plots as the annealing temperature is increased, which shows that Er_2O_3 (E) and TiO_2 react to form the ETO. There is another phase change that takes place in the titania, however. The anatase (A) titania feature at $2\theta=25^\circ$ is significantly smaller for the sample annealed at 1050 °C, as compared to the sample annealed at 1000 °C. At the same time, the rutile (R) titania feature at $2\theta=27.5^\circ$ becomes much more intense.

For the lower doping level (nominal Er:Ti atomic ratio of 0.067), the ETO phase only becomes a minor component of the nanofibers, presumably because not enough erbium is present to combine with titanium, as shown in panel (c) of Fig. 1. Although the rutile phase shows behavior similar to that with the higher doping ratio, the anatase phase is not diminished nearly as much, if at all, after 1050 °C annealing.

DRIFTS shows that annealing the erbia powder alone had little or no effect on the near-infrared absorption bands characteristic of the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ electronic transitions in Er^{3+} , as shown in the top of Fig. 2. This is not surprising when considering that the crystal structure remains essentially unchanged. For the erbia doped titania nanofibers, the shape of the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ IR absorption band changes for different annealing temperatures, as shown in panels (b) and (c) of Fig. 2. The shape of the IR absorption bands has been attributed elsewhere to the Stark effect,¹⁰ so the spectral shape changes illustrated in panels (b) and (c) of Fig. 2 can be attributed to the changes in the local crystal field experienced by the Er^{3+} ions. It is interesting to note that the shape changes and positions of maximum intensity in near-IR spectra appear to be similar for the Er:Ti=0.54 and 0.067 doping levels in panels (b) and (c), respectively. This is consistent with the idea that the transition to the ETO structure is what causes the changes in the IR spectra; XRD shows that the erbia is transformed into ETO for both of the doping levels, and the presence of “extra” titania in the fibers doped with a smaller amount of erbia appears to be of little consequence in terms of the nature of the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ transition in the erbium ions. As a control, IR absorption spectra were collected for titania nanofibers which were not doped with erbia. No features were found near the 6500 and 10 300 cm^{-1} spectral regions.

The changes in absorption spectra in panels (b) and (c) of Fig. 2 are of interest for a few reasons. First, they demonstrate that the location of the most intense feature can be changed. For nanofiber samples annealed at 800 and 900 °C, the most intense peak is located at 6511 cm^{-1} (1536 nm), while for samples annealed at 1000 and 1050 °C the most intense peak is at 6539 cm^{-1} (1529 nm). The effect of annealing temperature on the location of the maximum spectral intensity is likely due to changes in the local environment of the Er^{3+} ions.

A second reason that the changes in absorption spectra in panels (b) and (c) of Fig. 2 are of interest is that it shows that

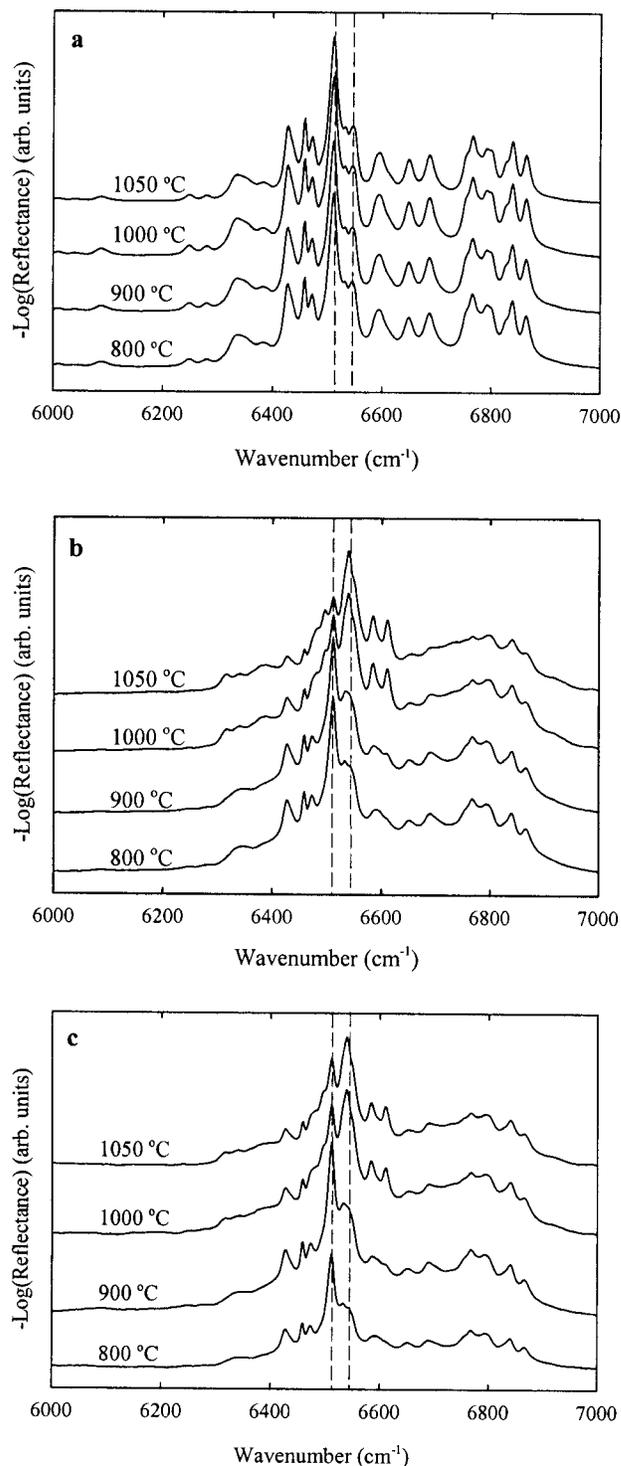


Fig. 2. Near-IR spectra at four annealing temperatures of (a) erbia powder, (b) erbia doped titania nanofibers with a nominal atomic ratio of Er:Ti = 0.54, and (c) erbia doped titania nanofibers with a nominal atomic ratio of Er:Ti = 0.067. The vertical dashed lines are drawn at 6513 and 6545 cm^{-1} to guide the eye (see text).

the width of the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ spectral feature can be modified by changing the local environment of the Er^{3+} ions. A quantitative measure of the width of the features can be calculated using a simple procedure outlined by Nazabal *et al.*¹⁵ and was done here for the Er:Ti=0.54 doping level. The

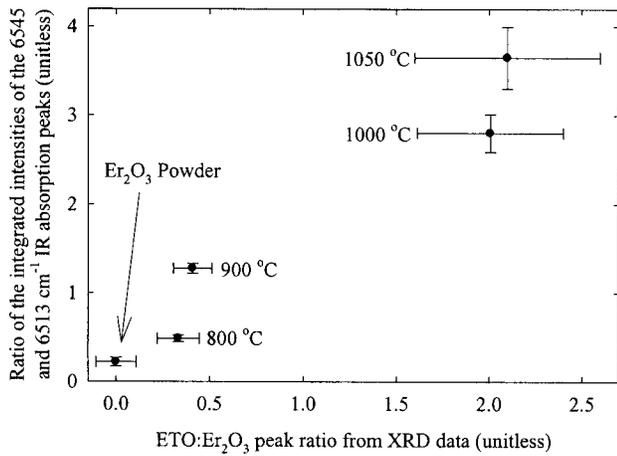


FIG. 3. Relationship between the ratio of the integrated intensities of the 6545 and 6513 cm^{-1} IR features and the ETO:Er₂O₃ peak ratio from XRD data.

paper by Nazabal *et al.* was concerned with applications in IR lasers, fiber optic amplifiers, etc., and in that field the traditional unit used in spectra is nanometers instead of cm^{-1} . Accordingly, the so-called effective absorption bandwidths were calculated from the spectra in the middle of Fig. 2 and the results are 44.4, 46.0, 53.6, and 47.5 nm (± 1 nm) for the annealing temperatures of 800, 900, 1000, and 1050 °C, respectively. This trend in the bandwidths could arise if the location of the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ near-IR bands for erbia and ETO were slightly different, so mixtures of the two phases would result in spectral broadening. Based on these results and the previous work by Nazabal *et al.*,¹⁵ a material which contains Er³⁺ in a mixture of environments might result in a larger bandwidth as compared to materials with only one dominant environment for the Er³⁺.

To investigate the connection between the environment of Er³⁺ and the nature of the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ electronic transitions, the IR spectra in panel (b) of Fig. 2 and the XRD patterns in panel (b) of Fig. 1 were fit with Lorentzian peaks. Two IR features which appear to be strongly affected by the annealing temperature are a pair of peaks near 6513 cm^{-1} and another single peak near 6545 cm^{-1} . The former is diminished in transitioning from erbia to ETO while the latter is enhanced. The ratios of the integrated intensity of these two features is plotted against the ratios of XRD features for ETO and erbia, in Fig. 3. All ratios in this figure used the feature associated with ETO as the numerator. There does appear to be a relationship, with a monotonic increase in the ratio of the 6545–6513 cm^{-1} IR peaks with increasing ETO:Er₂O₃ ratio determined from the XRD data. This relationship is again consistent with the idea that the crystal structural changes alter the near-IR spectra. In Fig. 3, erbia powder was used for a reference spectrum with 100% erbia in the absence of ETO. The uncertainty bars were estimated using the root-mean-square error from the peak fitting algorithm.

For completeness, the IR features associated with the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ electronic transition in Er³⁺ are shown in Fig. 4. Again, for erbia powder, the annealing temperature seems

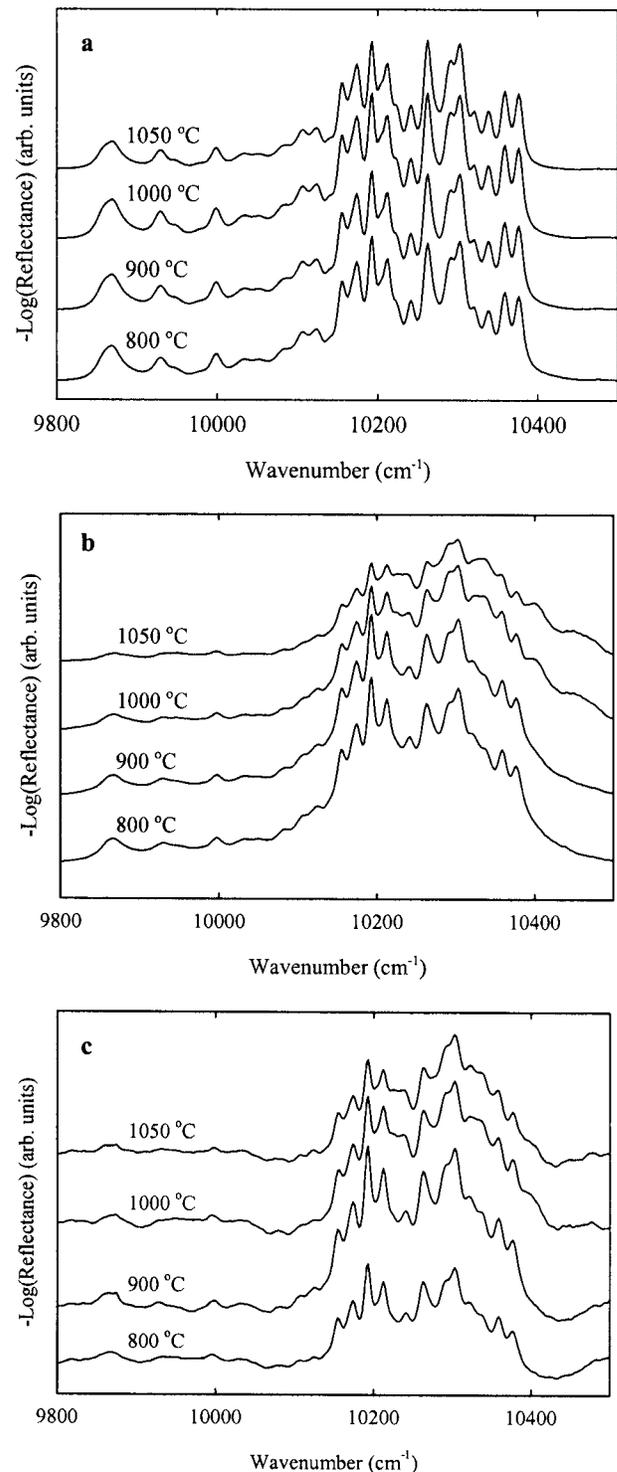


FIG. 4. Near-IR spectra at four annealing temperatures of (a) erbia powder, (b) erbia doped titania nanofibers with a nominal atomic ratio of Er:Ti = 0.54, and (c) erbia doped titania nanofibers with a nominal atomic ratio of Er:Ti = 0.067.

to have little effect on the shape of the absorption bands, as shown in panel (a). The shape of this IR absorption band for materials doped with an atomic ratio of Er:Ti = 0.54 and 0.067 shown in panels (b) and (c), respectively, appear to be less affected, as compared to the corresponding changes in

the 6500 cm^{-1} band shown in panels (b) and (c) of Fig. 2. An interesting relationship between the XRD peak ratios and these FTIR spectra involves the ratio of the total integrated intensity of the ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$ and ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ ($10\,300$ and 6500 cm^{-1}) bands. There appears to be a monotonic decrease in the total intensity of the $10\,300\text{ cm}^{-1}$ band relative to the 6500 cm^{-1} band as Er_2O_3 is transformed into ETO. The ratios of the integrated intensities of these bands have been shown to change in similar material systems elsewhere using cathodoluminescence, and the affect was attributed to symmetry changes.¹⁰ It is therefore reasonable to propose that the changes reported here in panels (b) and (c) of Fig. 4 are also due to changes in the local crystal field experienced by the Er^{3+} ions.

The shape changes of near-IR absorption spectra is of interest for optical devices but it may also have significance for TPV. The amount of energy that an Er^{3+} doped material can radiate during heating is determined by its spectral emissivity and temperature. The emitted power is proportional to the integral of the product of the spectral emissivity of the material and the Planck blackbody energy distribution function. Thus, power density can be enhanced by increasing the emissivity in a certain band or by increasing its bandwidth. It is reasonable to hypothesize that the power density of a selective emitter could be enhanced by mixing materials with different Er^{3+} states. It should be emphasized, however, that room temperature absorption spectra are not necessarily indicative of the thermal emission spectra at temperature, so thermal emission measurements are needed to test this hypothesis. This testing is the main focus of our ongoing studies of rare-earth doped metal oxide nanofibers.

IV. SUMMARY

We have demonstrated the synthesis of erbia doped titania nanofibers and have investigated the affect of annealing temperature on the crystal structure and near-IR absorption spectra of these materials. We have shown that annealing these titania nanofibers doped with erbia powder results in the reaction of titania and erbia to form the ETO pyrochlore phase, and that the extent of this reaction increases with annealing

temperature. Moreover we have shown that the shapes of the near-IR absorption bands change depending on the extent of this reaction, and we propose that these changes are most likely the result of changes in the local environment of the Er^{3+} ions. The differences in the near-IR absorption bands of these materials may be relevant for TPV applications because some of them may exhibit a larger selective emission bandwidth than others. To test this hypothesis, emission spectra need to be recorded instead of absorption spectra, and this is the focus of our ongoing studies on these materials. In general, control over the absorption bandwidth is also relevant for IR laser, fiber optic, and near-IR night vision applications.

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