Upconverting Nanophosphors for High Temperature Applications

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ABSTRACT

Upconverting nanopowders of rare earth (RE) doped refractory oxides were synthesized through a wet chemical route. Temperature sensitive characteristics over the range of 300K to 1700K with excellent sensitivity were demonstrated with the upconverting phosphors. The results indicate that the upconverting phosphor thermometry approach is promising for remote and accurate monitoring of thermal barrier coating (TBC) temperature and "health" conditions.

Keywords: upconverting phosphor, nanopowder, refractory oxides, temperature, sensing

1 INTRODUCTION

To realize efficient power generation in gas turbine engines, higher combustion temperatures are targeted. This presents an urgent need for experimental techniques suitable for accurate and in-situ monitoring of temperature and the "health" condition of the thermal barrier coating on a blade or vane in a combustion environment, where conventional techniques are difficult to be applied [1], [2].

Phosphor thermometry has been recognized as promising for such an application. Nonetheless, the widely researched down conversion route has reached the temperature-sensing limit at about 1800 K and is difficult to be further improved [3]. In a down conversion approach, the phosphors are mostly excited at ultraviolet (UV) wavelengths. UV excitation tends to be problematic in large-scale facilities because it demands not only expensive and dangerous UV lasers but also costly UV-quality windows. Meanwhile, UV radiation is absorbed or scattered by the combustion gases and the upper coating layers before reaching the phosphors, resulting in diminished luminescence efficiency, i.e., limited temperature sensing capabilities. Here we report on a unique upconverting phosphor thermometry technique, which is developed for overcoming the difficulties encountered in the conventional down-conversion phosphor approaches.

On the other hand, researchers have found that using nanoparticles as feeding materials for plasma spray of TBC is advantageous in TBC quality control [4]. In this work, efficient upconverting thermographic nanophosphors are developed via a simple and low-cost wet chemical co-precipitation synthesis technology. The major advantage of this technology is that the control of stoichiometry is at the atomic level that provides the opportunity to create function-specific materials with great reliability. This technology has been demonstrated to be excellent for not only fabricating mono-dispersed nanoparticles, but also for achieving significantly higher doping concentration quenching threshold that is essential to the enhancement of the upconversion effect.

2 EXPERIMENTAL

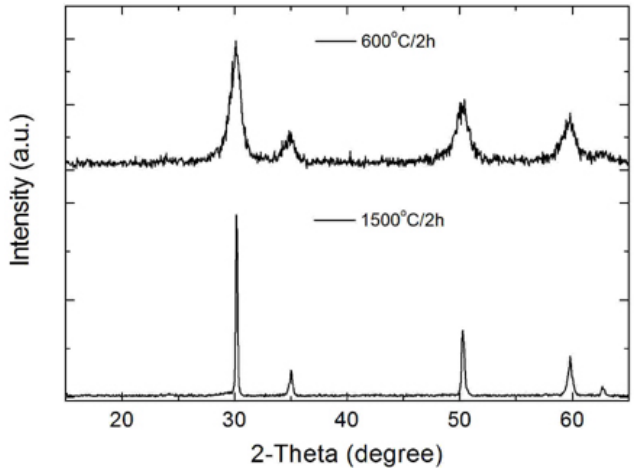
In this study, several refractory oxide material systems with RE doping were examined, including the current TBC material of choice, YSZ (8wt.% yttria stabilized zirconia), and materials for possible future TBC applications (zirconate pyrochlores and rare earth silicates). RE doped or co-doped Y_2O_3, YAG, YSZ, Lu_2O_3, as well as zirconate pyrochlores and lanthanide silicates fine powders were fabricated through a co-precipitation process. Analytical reagents of nitrates were used as starting materials; ammonia and ammonium hydrogen carbonate or urea was used as the co-precipitant. In a typical experiment, stoichiometric amounts of nitrates were dissolved in deionized water and ethyl alcohol to form a 0.1M solution. Diluted ammonia and ammonium hydrogen carbonate solution was dropped into the above solution under vigorous stirring at room temperature until the pH value of the solution reaches 8-9. The solution was stirred at least 2 hours for aging. Powders were collected through the vacuum filtration and washing process. Then the powders were dried at 60ºC over night. Heat-treatments were carried out after drying in order to convert the powders into oxides.

3 RESULTS AND DISCUSSION

3.1 Characterization of the Nanopowders

The crystallinity of the nanophosphors was characterized by means of X-ray diffractometer (XRD) and the morphologies of nanopowders were observed using transmission electronic microscopy (TEM, Joel 2010) and scanning electron microscopy (SEM). The analyses results indicate that well dispersed nanophosphors have been

obtained and the particle sizes can be controlled by the calcine temperature and duration times. Strong upconversion luminescence emissions were observed in most of the materials. Effects of precursors, doping concentration and matrix composition on luminescence properties were examined and it was found that curtain precursors and co-dopants were beneficial for the upconversion efficiency enhancement.



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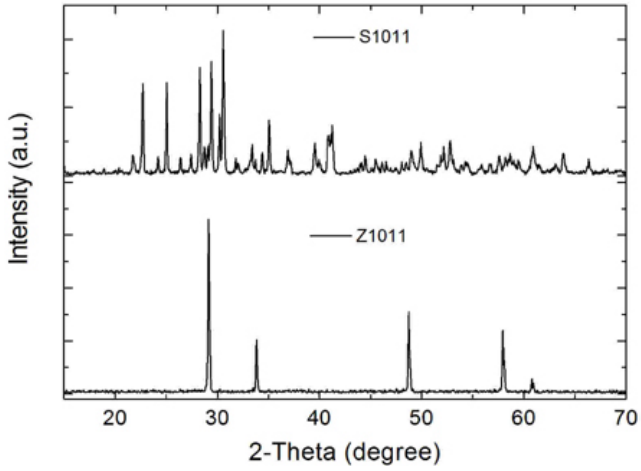

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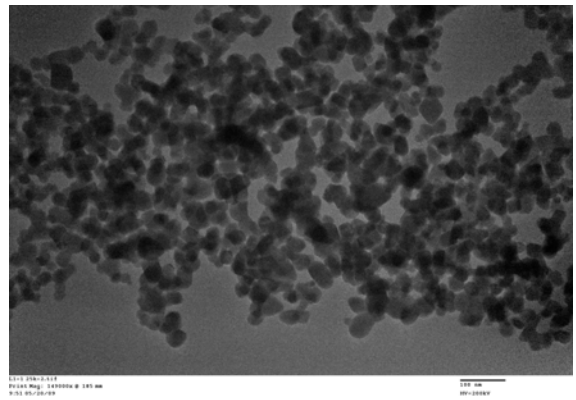
Figure 1. XRD patterns of the RE doped (a) YSZ powders and (b) zirconate pyrochlore and lanthanide silicate powders.

Shown in Figure 1(a) are the XRD patterns of the RE doped YSZ powders sintered at different temperatures. RE doped YSZ powders sintered at 600ºC have been crystallized and exhibit upconversion effect under a 970 nm laser excitation. Average nano-crystallite sizes are extracted from the XRD data using Scherrer's equation as 20 nm and 100 nm in the 600ºC and 1500ºC calcined samples, respectively. Shown in Figure 1(b) are the XRD patterns of RE doped zirconate pyrochlore (Z1011) and lanthanide silicate (S1011). The formation of the nano-crystallites in the samples sintered at 850ºC has been confirmed. The non-agglomeration and uniform size distribution feature of the nanopowders are demonstrated by TEM and SEM observations, as shown in Figure 2. The results indicate that nanopowders with desirable characteristics have been obtained.



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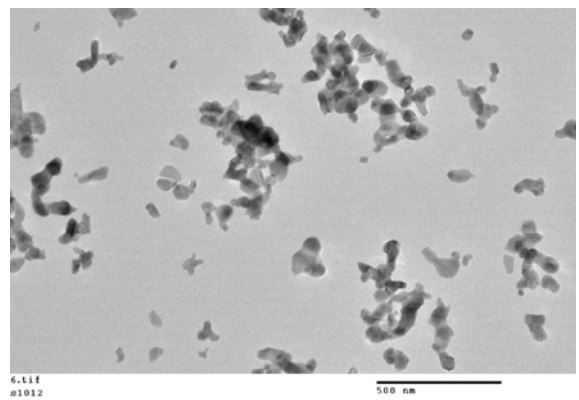

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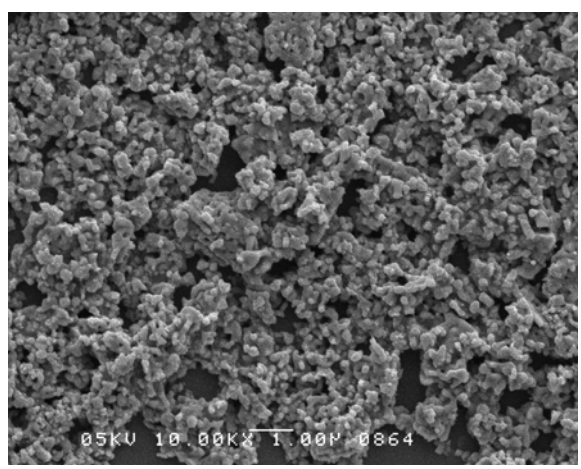
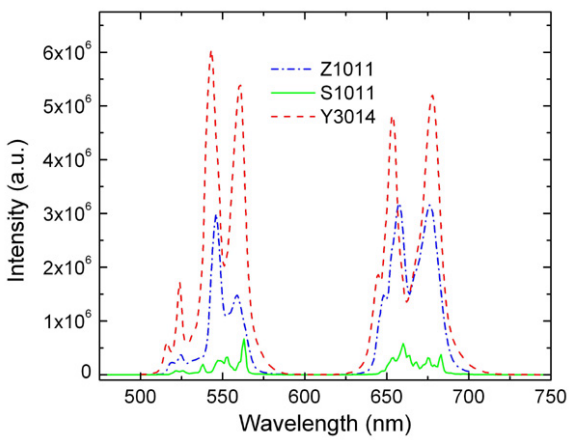


(c)

Figure 2 TEM images of RE doped nanopowders of (a) Lu_2O_3 (the bar at lower right corner indicates 100 nm); (b) S1012 (the bar indicates 500 nm); (c) SEM image of YAG nanopowders (the bar indicates 1 μm).

3.2 Room Temperature Upconversion Luminescence Measurement

The nanopowders were cold pressed into pellets and sintered at different temperatures in air for optical measurements. Room temperature upconversion properties of the samples were investigated and some typical upconversion emission spectra are shown in Figure 3. A 970 nm centered CW diode laser was employed as the excitation source. The spectrometer used to record the upconversion emissions was NanoLog from Horiba Jobin Yvon. The luminescence from most of the samples at room temperature could be seen by the naked eye in a dark room.



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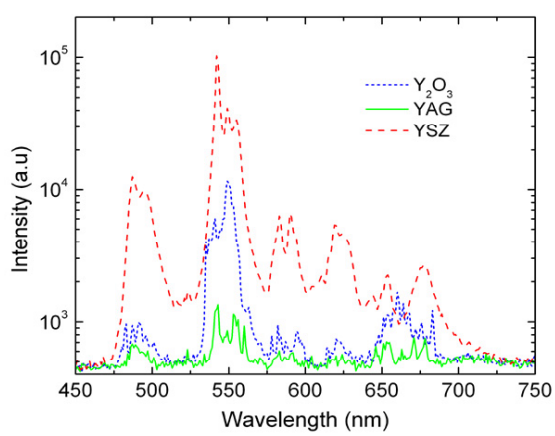


(b)

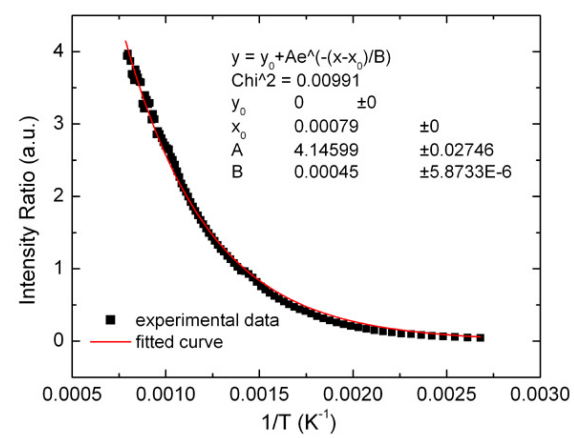
Figure 3. Room temperature upconversion emission spectra of RE doped oxides.

Shown in Figure 3(a) are upconversion emission spectra of RE doped zirconate pyrochlore and lanthanide silicate samples compared to that of the RE doped YSZ sample. Although the zirconate and silicate samples were studied in this work without optimizing their composition and doping configuration, the samples exhibit comparable upconversion effect with the YSZ at room temperature. In one doping configuration, the upconversion emission intensities of RE doped YSZ samples are on the same order with those of RE doped yttria and lutetia. While in another doping configuration, YSZ as host matrix is superior to yttria and YAG in terms of the upconversion effect (as shown in Figure 3(b)).

3.3 High Temperature Sensing Properties

To verify the high temperature sensing concept of upconverting phosphors, both fluorescence intensity ratio (FIR) and lifetime approaches were adopted. In the FIR approach, a 970nm CW diode laser is used as the excitation light source. Considering the effect of black body radiation at high temperatures, an optical chopper and two lock-in amplifiers were employed to obtain luminescence signals amid the radiation background. A coiled heater from ZIRCAR Ceramics was used as a heating source, which has a maximum temperature limit of 1373 K. A thermocouple was employed to record the sample temperature and was placed in contact with the samples.

The temperature sensing data obtained via FIR approach is shown in Figure 4. One can see that the temperature sensitivity data obtained through the FIR technique remains very high even when the temperature is up to 1200 K. The maximum sensitivity in RE doped yttria at 1100K was determined as $0.006K^{-1}$.



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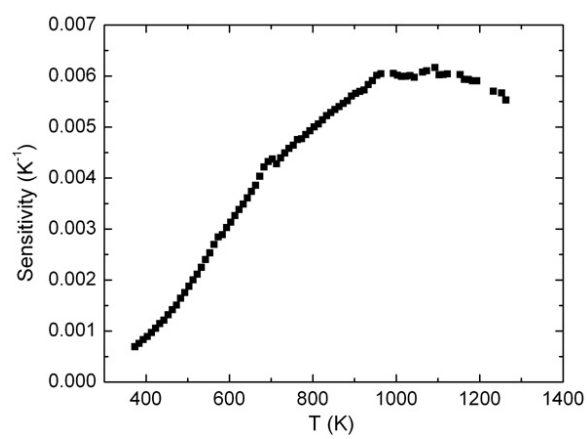

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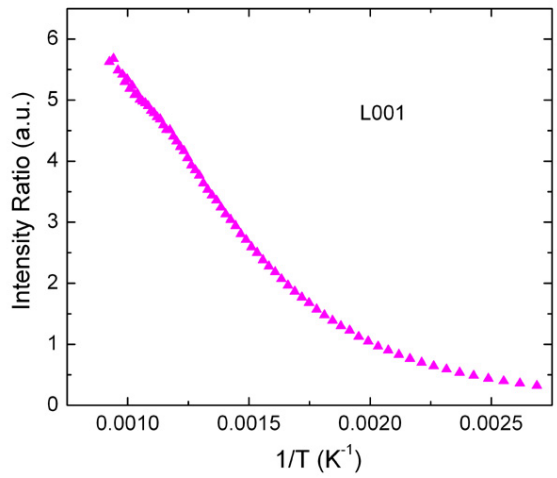

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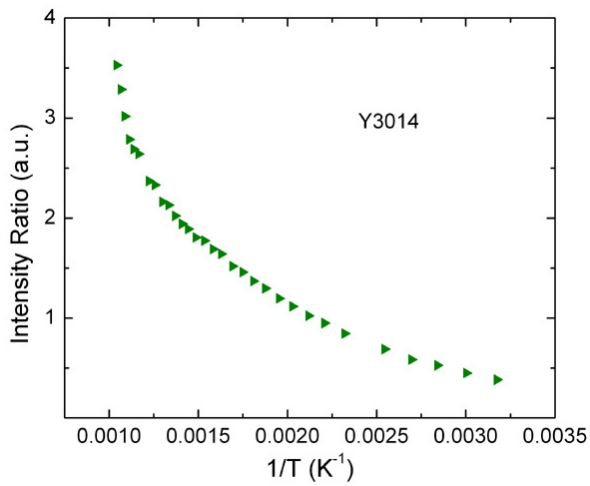

(d)

Figure 4. (a) FIR experimental data and its fitting curve and (b) temperature sensitivity of RE doped yttria; FIR versus temperature with RE doped samples of (c) Lu_2O_3; (d) YSZ.

For the decay time series experiments, only the RE doped yttria sample was tested due to its high yield found in the preliminary work. Pulsed Nd:YAG excitation with 10 ns pulse duration and 1064 nm wavelength was compared to excitation with a pulsed xenon flashlamp with 2 µs pulse duration (Perkin-Elmer LS 1130 Flashpac). The emission from the flashlamp is broadband and overlaps the dominant absorption band of the phosphor near 970 nm. The variation of the luminescence lifetime of the sample with temperatures ranging from 300 K to 1700 K is shown in Figure 5. One can see that the luminescence lifetimes exhibit a monotonic decrease with increasing temperature. The lifetime varies from about 300 µs to 125 µs over the temperature range of 300 K to 1700 K. These results suggest that the lifetime technique with pulsed Nd:YAG excitation is very promising as it demonstrates excellent temperature sensitivity. Figure 5 also shows that flashlamp excitation results in an even greater temperature sensitivity. The ability to achieve high temperature sensitivity with a non-coherent pulsed light source such as a flashlamp is encouraging for applications where lasers are not desirable.

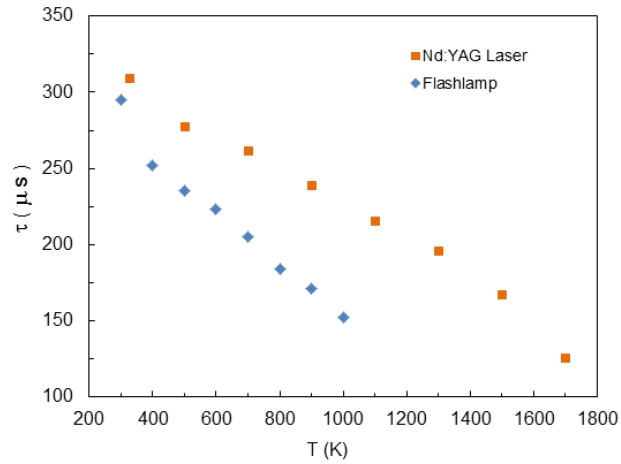

Figure 5. Variation of the luminescence lifetime with temperature for RE doped yttria sample, which was excited with a 1064nm short-pulsed Nd:YAG laser pulsing at a rate of 10 Hz and a xenon arc flashlamp pulsing at 25 Hz.

4 CONCLUSION

Upconverting thermographic nanophosphors were developed via a co-precipitation synthesis technology with desired features of non-agglomeration and uniform size distribution. Both of intensity ratio and lifetime approaches were adopted to verify the high temperature sensing concept of the upconverting phosphors. Temperature sensing capability up to 1700K in RE doped refractory oxides was demonstrated with excellent sensitivity. These development efforts show promise of a novel approach for accurate and non-contact gas turbine surface temperature and "health" condition monitoring.

5 ACKNOWLEDGEMENT

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