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Temperature sensing with fluorescence intensity ratio technique in epoxy-based nanocomposite filled with Er^{3+}-doped 7YSZ

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ABSTRACT

Luminescent nanocomposite of epoxy filled with Er^{3+}-doped yttria-stabilized zirconia (7YSZ) is prepared with their luminescence spectra measured in the temperature range 123–423 K. Fluorescence intensity ratio (FIR) of the two Er^{3+} emissions is also obtained in the same temperature range. Er–7YSZ/epoxy nanocomposites exhibited higher sensitivity of 0.18%/K as compared with the bare Er–7YSZ particles. Luminescence thermometry is demonstrated by using the nanocomposites as temperature sensitive paint (TSP) with a resolution of 1 K. The advantage of FIR technique combined with the excellent thermal stability of epoxy matrix makes the Er–7YSZ/epoxy nanocomposites viable as temperature sensitive paint for aerodynamic applications.

1. Introduction

Luminescence thermometry is a versatile as well as robust optical technique for temperature sensing [1]. Temperature is determined by measuring the temperature-dependent changes in luminescence properties of a luminescent material. A number of luminescence materials, such as (CdSe)ZnS quantum dots [2], Eu-doped yttria-stabilized zirconia [3], Cr^{3+}-doped yttrium aluminum borate [4], have been explored for their temperature-dependent luminescence intensity. As the luminescence intensity collected by the detector is determined by not only their intrinsic temperature-dependence but measurement conditions i.e., luminescence loss and the fluctuation in the power of exciting laser, etc., the temperature–luminescence intensity curve thus has to be precalibrated to a high accuracy with careful control of measurement conditions to ensure the precise measurement of temperature. Luminescence lifetime on the other hand is the luminescence characteristics that is not seriously influenced by measurement conditions. Luminescence thermometry based on lifetime-temperature dependence is considered a self-referenced and thus more robust technique for temperature sensing. A progress review on doped oxide materials for luminescence thermometry, particularly thermometry based on lifetime-temperature dependence, has recently been made by Chambers and Clarke [5]. As a combined approach, both luminescence intensity and lifetime of $La_2O_2S:Eu^{3+}$ are used as dual temperature probe by Omrane et al. for better accuracy [6]. Another alternative to luminescence intensity or decay lifetime is the intensity ratio between the emission bands from thermally-coupled electronic transitions [7,8]. Of particular interest is the temperature sensor based on the fluorescence intensity ratio (FIR) of Er^{3+}–Yb^{3+} codoped materials. By measuring the fluorescence intensity from the temperature-dependent transitions of Er^{3+}, i.e., $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$, temperature is obtained with less dependence on measurement conditions, i.e., luminescence loss and the fluctuation in the power of exciting laser.

By incorporating temperature sensitive particles in polymer matrices, temperature sensitive paint (TSP) was first prepared in the 1950s [9] and has received considerable attentions since then [10,11]. Capable of being applied to complex surfaces at low temperatures, TSPs are of critical importance in aerodynamics and fluid mechanics for the measurements of surface temperatures [12], gas pressure or velocity of fluids [13]. Temperature sensitive dyes, such as rhodamine dyes [10], or europium thenoyltrifluoroacetonate (EuTTA) [14], have been intensively studied for their temperature-dependent luminescence intensity in TSPs. Sensing of temperature with TSPs filled with these temperature sensitive dyes has been demonstrated in the temperature range of 273–320 K. In parallel to the TSPs based on luminescence intensity-temperature dependence, there are also efforts of making TSPs based on luminescence lifetime-temperature dependence. TSPs activated with tris(β-diketonate) phenanthroline europium complex [15], ruthenium tris-1,10-phenanthroline [16], iridium(III) complex [17], etc. have been prepared with their lifetime-temperature dependences being used as temperature probes. These TSPs are not only capable of measuring temperatures but their lumi-

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nescent sensitivities to oxygen partial pressure make them dual-sensors for both temperature and pressure. TSPs based on fluorescence intensity ratio (FIR) technique is still yet to be developed, especially TSPs that could be used under cryogenic conditions.

In this contribution, we explored the use of Er^{3+}-doped yttria-stabilized zirconia (Er–7YSZ) as temperature sensitive material in a TSP based on epoxy. Er^{3+}-doped yttria-stabilized zirconia has been studied as temperature sensors in thermal barrier coatings for the past few decades. Temperature was obtained from the pre-calibrated FIR-temperature curve of Er^{3+} in the temperature range of 123–423 K.

2. Experimental

The Er–7YSZ powders (with the stoichiometric formula of $Er_{0.015}Y_{0.055}Zr_{0.93}O_{1.965}$) were synthesized by a reverse co-precipitation method, which has been described in detail in previous contributions [18]. Particles obtained after the final heat treatment at 1200 °C for 2 h were subjected to ball-milling for another 24 h. The sizes of the particles thus obtained were ~100 nm. The content of Er–7YSZ particles in the final TSP was 50 wt% in order to maintain the processibility of epoxy matrix. For the preparation of temperature sensitive paint, Er–7YSZ particles were first homogeneously dispersed in epoxy resin (TED85) by mechanical stirring followed by ultrasonicating. Acetone was also added in the mixture to adjust the viscosity of the slurry. Diethylenetriamine (DETDA) was then added as curing agent for *in situ* polymerization of epoxy. For luminescence measurements, TSP coatings were fabricated by applying the composite slurry on glass slides with razor blades. The coatings were completely dried at 70 °C for 8 h in an oven and the final thickness of the coatings were ~50 μm.

Luminescence properties of the coatings were measured at the excitation with an Argon ion laser of 488 nm (Coherent, Santa Clara, CA) and collected with a microscope-based Raman spectroscopy system (Labram HR, Horiba, NJ). Luminescence spectra were also collected through the same Raman spectrometer in the luminescence mode. The laser was operated in the "power-track" mode and the output power was set at 20 mW with power fluctuation of ±0.5%, as calibrated both by the built-in power meter of the laser and an external power meter (FieldMax, Coherent, Santa Clara, CA). A 10× objective lens was used for both Raman and luminescence measurements with a spatial resolution of ~3 μm for all the measurements. For the measurement of temperature-dependent luminescence spectra, a small portion of sample was cut in order to fit into the crucible of a heating stage built for an optical microscope (TS1500EV-6, Linkam Scientific Instruments Ltd., UK). Luminescence spectra were collected in the temperature range 123–423 K at an interval of 25 K. In account for the possible errors introduced by chemical inhomogeneity, luminescence signal from five spots on the sample were collected and averaged at each temperature of interest.

For the measurement of fluorescence intensity ratio, the luminescence band profiles of $^2H_{11/2} \rightarrow {}^4I_{15/2}$ (noted as H-band, here after) and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (as S-band) transitions were fitted to mixed Gaussian–Lorentz equations. Due to the difficulty in separating $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition (535–553 nm) from the $^2H_{11/2} \rightarrow {}^4I_{13/2}$ transition (553–580 nm), peak-fittings were performed in the range 535–580 nm with the $^2H_{11/2} \rightarrow {}^4I_{13/2}$ transition included. For consistency, the number and position of the peaks used for the fitting of the luminescence bands (as indicated by asterisks in Fig. 1 and listed in Table 1) were fixed for all the samples at all temperatures measured. The integrated intensities under the luminescence peaks were determined in the range of 510–535 nm for H-band, and 535–553 nm for S-band, and were noted as I_H ($^2H_{11/2} \rightarrow {}^4I_{15/2}$) and I_S ($^4S_{3/2} \rightarrow {}^4I_{15/2}$). The fluorescence intensity ratio (FIR) was then determined as $FIR_{HS} = I_H/I_S$.

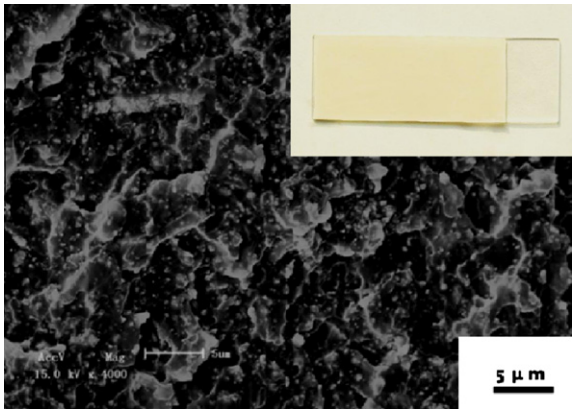

Fig. 1. Cross-sectional SEM image of Er–7YSZ/epoxy nanocomposite with 50 wt% of Er–7YSZ. Shown in the inset is the photo of the temperature sensitive paint of Er–7YSZ/epoxy cast on a glass slide.

Table 1
Assignment and wavelength of peaks used for peak-fitting.

Electronic transitions	Wavelength (nm)					
$^2H_{11/2} \rightarrow {}^4I_{15/2}$	514.8	516.4	517.8	522.5	523.1	524.1
	525.0	526.2	532.1			
$^4S_{3/2} \rightarrow {}^4I_{15/2}$	539.4	541.4	542.2	543.7	544.6	544.9
	545.2	547.1	548.0	552.9		
$^2H_{11/2} \rightarrow {}^4I_{13/2}$	557.5	559.2	560.1	562.4	563.0	

3. Results and discussion

XRD and Raman spectroscopy (not shown here) confirmed that the Er–7YSZ particles obtained by the reverse co-precipitation method have a *t*-prime tetragonal structure. The long-time ball-milling process not only reduced the particle size to nanometer scale but the agglomeration of Er–7YSZ particles was suppressed. Homogeneous dispersion of Er–7YSZ particles in epoxy matrix was achieved, as shown in the cross-sectional SEM image (Fig. 1). Also can be seen from the microstructural image was that no voids or holes were present even at this high loading of Er–7YSZ for 50 wt%. Surface roughness of TSP is also of importance in aerodynamics applications in that small surface roughness, i.e., smoother surface, minimizes the disturbance of TSP to the air flow. In our case, the surface roughness was ~0.4 μm, as determined by Atomic Force Microscope (AFM) analysis, which is desirable for TSPs in aerodynamic applications.

The luminescence spectra of Er–7YSZ/epoxy nanocomposite films at temperatures of 123 K, 273 K, 423 K were shown in Fig. 2. There are three principle luminescence bands, which can be identified as being due to $^2H_{11/2} \rightarrow {}^4I_{15/2}$ (510–535 nm), $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (535–553 nm), $^2H_{11/2} \rightarrow {}^4I_{13/2}$ (553–580 nm) transitions. Fine structures were observed in all the luminescence bands. The emission bands were deconvoluted into fine peaks by fitting of band profile to mixed Gaussian–Lorenzian equations. By fitting of the data to mixed Gaussian–Lorentz equation, the integrated intensities were obtained and noted as IH ($^2H_{11/2} \rightarrow {}^4I_{15/2}$) and IS ($^4S_{3/2} \rightarrow {}^4I_{15/2}$). The fluorescence intensity ratio (FIR) was then defined as FIRHS = IH/IS. Compared with Er–7YSZ powders, no shift of positions of the three luminescence bands in the composite film was observed at elevated temperatures. The FIR of the two emission bands increased consistently with temperature, indicating increased population of the $^2H_{11/2}$ level. At elevated temperatures, electrons on the $^4S_{3/2}$ level could be thermally excited into the upper level of $^2H_{11/2}$ by crossing a small energy gap, giving rise to the thermal population of $^2H_{11/2}$ level. The two