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Effects of Reducing Atmosphere on the Luminescence of Eu³⁺-Doped Yttria-Stabilized Zirconia Sensor Layers in Thermal Barrier Coatings

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The use of Eu³⁺-doped yttrium-stabilized zirconia (YSZ) as an embedded layer in thermal barrier coatings for luminescence temperature sensing has previously been demonstrated in air. In this work the effects of exposure to reducing atmospheres on the luminescence spectra and luminescence lifetime as a function of temperature are reported. No effect of reducing atmosphere, down to oxygen partial pressures (P_{O_2}) of $<10^{-11}$ ppm, on either the Eu³⁺ luminescence spectrum or the luminescence lifetime up to 900°C are seen although the overall luminescence intensity is decreased. The insensitivity of the temperature dependence of the luminescence lifetime to oxygen partial pressure indicates that Eu³⁺-doped YSZ based temperature sensors can be used with confidence in reducing as well as in air atmospheres. The results also suggest that the charge transfer mechanism responsible for the temperature dependence of the luminescence lifetime is unaffected by the oxygen vacancies introduced by reduction.

I. Introduction

THE measurement of temperature using luminescence techniques, sometimes referred to as luminescence thermometry, has been studied since the early 1950s.[1,2] Of the various thermometry methods, the most reliable, physically based method is the measurement of the luminescence decay lifetime, following pulsed-laser excitation. In this method the temperature is obtained by comparing the measured lifetime to a previously calibrated luminescence lifetime-temperature dependence curve. One of the new applications of luminescence thermometry is the noncontact measurement of temperatures in thermal barrier coatings. These are used in gas turbines to provide thermal insulation to super alloys and enabling them to operate at higher temperatures and hence higher energy efficiency than without coatings. Because the materials used in thermal barrier coatings, such as yttria-stabilized zirconia and gadolinium zirconate, are not themselves luminescent, the use of rare-earth ions in solid solution within these coating materials has been investigated in detail. Because thermal barrier coatings are deposited by electron-beam evaporation or plasma spraying, it has proven possible to also embed the rare-earth ions at specific, predetermined locations within the coatings during deposition. Recently, we have demonstrated an ability to monitor the temperature both at the surface of a coating and at the interface between TBCs and the underlying alloy up to 1100°C in a temperature gradient by embedding Eu³⁺ ions at these locations during TBC deposition.[3] Although several different rare-earth-doped yttria-stabilized zirocnia have been studied[4] and have distinctive characteristics, Eu³⁺-doped 8 m/o $YO_{1.5}$ zirconia (8YSZ)

seems to be the most promising for temperature sensing of TBCs due to its superior combination of luminescent properties. In addition, the luminescence from Eu³⁺-doped 8YSZ is unaffected by large thermal gradients, repeated thermal cycling to 1150°C, or long-term, high-temperature annealing.[5,6] These studies and demonstrations were performed at atmospheric pressure and in air. However, during gas turbine service as well as in other potential applications, such as in rocket engines, it is very possible that the TBCs and any embedded luminescence sensor layers could be exposed to low oxygen partial pressures. Although thermographic phosphors are usually regarded as being insensitive to pressure,[7] there are reports of possible oxygen quenching of the luminescence of the pressure-sensitive paints (PSPs) used in wind tunnel studies.[8] Furthermore, zirconia is known to darken when partial reduced because of the formation of point defect clusters so there is reason to believe that this may affect the luminescence decay processes. This is especially so because there is evidence that the luminescence lifetime from Eu³⁺-doped phosphors is determined by charge transfer (CT).[4,9,10] For these reasons, we have investigated the effect of different oxygen partial pressures on the luminescence from Eu³⁺-doped 8YSZ sensor layers. Oxygen partial pressures (P_{O_2}) down to 10^{-11} ppm have been explored as well as the reversibility under repeated oxidation–reduction heat treatments. Although these partial pressures are much lower than occur in air-breathing engines, they were nevertheless investigated to explore the effects of extreme reduction and its possible effect on the luminescence decay mechanism.

II. Experimental Procedure

The coatings investigated consisted of a 10 μm thick sensor layer of 1 at% Eu³⁺-doped 8YSZ, deposited by electron beam evaporation (EB–PVD) on top of a standard thickness (140 μm) EB–PVD 8YSZ thermal barrier coating. The coatings were on a 1 in. diameter (Ni, Pt)Al-coated superalloy coupon, typical of those used extensively for furnace cycle testing (FCT) of thermal barrier coatings.

Before reduction, the as-deposited coatings were first annealed in air at 1100°C for 4 h to assure complete oxidation of the zirconia. Then and after subsequent heat treatments, diffuse optical scattering measurements were made over the wavelength range of 220–2600 nm using a SHIMAZU UV-VIS_NIR spectrometer (Kyoto, Japan) with $BaSO_4$ as reference to quantify the spectral absorption. The luminescent studies were carried out using a frequency doubled (10 ns) pulsed Nd:YAG laser at a wavelength of 532 nm with the spectra recorded using an Ocean Optics USB2000 spectrometer (Winter Park, FL) and a digital oscilloscope. Two types of reducing heat treatments were employed, one *ex situ* in a standard furnace adapted for reducing atmospheres and the other *in situ* in a specially designed chamber in which coatings could be heated in a controlled atmosphere and the luminescence recorded simultaneously. The *ex situ* annealing treatments were performed in an alumina tube furnace with the sample in a high-purity alumina boat and the reducing atmosphere was achieved by flowing high-purity Argon gas with 5% hydrogen into the tube furnace. Titanium
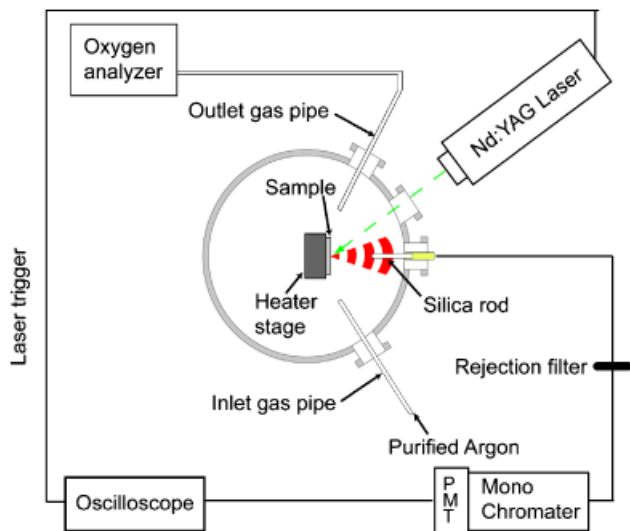
Fig. 1. Schematic of the controlled atmosphere chamber and the experimental setup used for the *in situ* luminescence measurements. The luminescence from the sample, shown schematically as the banded arc, is collected by the silica rod and fed into the fiber optic based system.

chips, also held in an alumina boat, were placed in the furnace upstream from the coated samples to getter residual oxygen in the flowing gas to achieve more reducing atmospheres. In this way, a reducing atmosphere with P_{O_2} of lower than 10^{-15} ppm could be achieved. The P_{O_2} was monitored by a zirconia oxygen sensor at the exit of the furnace. The *in situ* measurements were performed in a stainless-steel vacuum chamber in which the coating was mounted on the surface of a resistive heating stage that could be heated from room temperature to 900°C. Figure 1(a) frequency-doubled Nd:YAG laser with the wavelength of 532 nm was directed into the chamber through a UV glass window to excite the luminescence from the sensor layer on the surface of the coating. The luminescent signal was collected using a silica rod inside the chamber, which was connected with the fiber optics outside the chamber through an optical feed through. The collected light was sent to a photomultiplier tube whose output was recorded on an oscilloscope and spectrometer with the scattered laser filtered by a long-pass filter. The P_{O_2} in the chamber was monitored with an oxygen analyzer (Rapidox 2100, Cambridge Sensotec, St. Ives, Cambs, U.K.). All the measurements were made at a total chamber pressure of 1 atm but with different partial pressures of oxygen. For a P_{O_2} of 1000 ppm this was obtained using a metered mixture of high-purity nitrogen gas and air. To achieve lower values of P_{O_2}, the chamber was first evacuated and then filled with Argon gas with P_{O_2} of $\sim 10^{-11}$ ppm, achieved by purging the ultra high purity Argon gas from a gas cylinder through a gettering furnace (Centorr, Nashua, NH). A slightly positive total pressure was maintained at a flow rate of 0.5 L/min until the oxygen analyzer readout stabilized at about 10^{-11} ppm. The P_{O_2} was monitored throughout the measurements and indicated a fluctuation in P_{O_2} of $\pm 10\%$.

After each reducing atmosphere anneal, the coating was annealed in air for 4 h at 1100°C to fully reoxidize the zirconia.

The luminescence decay lifetime was determined by fitting the luminescent intensity to either a single or double exponential function of time

$$I = I_0 \exp(-t/\tau)$$
$$I = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2)$$
(1 and 2)

where I is the luminescent intensity and τ is the characteristic decay lifetime. (Over those temperatures where the intensity was better fit with a double exponential decay, the longer decay time was used to calibrate the lifetime-temperature curve.) The decay rate from the excited states is assumed to be the sum of a con-

stant, purely radiative emission rate $(1/\tau_R)$ and a temperature-dependent nonradiative component $(1/\tau_{nonR})$

$$1/\tau = 1/\tau_R + 1/\tau_{nonR}$$
(3)

where τ is the overall lifetime, τ_R and τ_{nonR} are the lifetime of radiative emission and temperature-dependent nonradiative emission.

Several models have been proposed to describe the luminescent lifetime-temperature dependence exhibited by a variety of materials. The multiphonon relaxation (MPR) model attributes the temperature dependence of lifetime to the nonradiative transfer of the excited energy to lattice phonons through a temperature-dependent phonon distribution. The nonradiative lifetime (τ_{MPR}) can thus be expressed as[11]

$$\tau_{MPR}(T) = \tau_{MPR}^0 \left[1 + \left(\exp \frac{h\omega}{2\pi kT} - 1 \right)^{-1} \right]^{-2\pi\Delta E/h\omega}$$
(4)

where τ_{MPR}^0 is the nonradiative decay rate at 0 K, ω is the frequency of the phonon mode involved, and ΔE is the energy gap between the excited and deexcited states.

For some other materials, the temperature dependence can be attributed to the thermal promotion of the excited electrons to a nonemitting electronic state followed by nonradiative relaxation. For europium phosphors, this nonemitting electronic state is usually considered to be a charge transfer state (CTS). Depending on temperature, the vibrational distribution of the excited states of the $4f$ electrons is determined by Boltzmann distribution. At high temperatures, a significant fraction of the distribution will be in resonance with the CTS. The nonradiative lifetime determined by CTS can then be expressed as[12]

$$\tau_{CTS}(T) = \left[cT^{*-1/2} \exp(-E_a/kT^*) \right]^{-1}$$
(5)

$$T^* = (h\nu/2k) \coth(h\nu/2kT)$$
(6)

The activation energy, E_a, represents the minimum energy classical crossing point for the initial and final state multidimensional potentials, and $h\nu$ represents the average energy of all the vibrational modes. The factor c is a collection of constants including the electronic coupling factor for the two states and the Stokes shift.

III. Results

The as-deposited coatings were white in color due to diffuse scattering and exhibited the characteristic photoluminescence spectrum of Eu^{3+} when excited at 532 nm consisting of two main peaks centered at ~ 590 and ~ 606 nm, corresponding to the transitions $^5D_0-^7F_1$ and $^5D_0-^7F_2$, respectively, with a weaker luminescence at ~ 635 nm, as shown in Fig. 2(b). Before reduction and after initial oxidation, the luminescence as well as the luminescence lifetime were measured in air up to 900°C using the system described in Chambers and Clarke.[6] The spectra and lifetime results were identical to those previously reported.[5,6] In the following sections, the effect of annealing in different partial pressures of oxygen are described on the room temperature luminescence properties and then on the high-temperature luminescence. After each reducing treatment, the luminescence and color of the coating could be recovered by the 4-h annealing in air at 1100°C.

(1) Room Temperature Luminescence
After annealing at an oxygen partial pressure of 2.3×10^{-15} ppm at 1100°C for 4 h, the coating darkened appreciably as shown in the micrographs in Fig. 2(a). There was also a decrease in the diffuse reflectance as shown in the same figure. The diffuse reflectance decreased from the fully oxidized state to the partially reduced state by a maximum of 19% in the UV-visible range. The decrease in diffuse reflectance indicated that the coating became more absorptive. A similar increase in absorption,
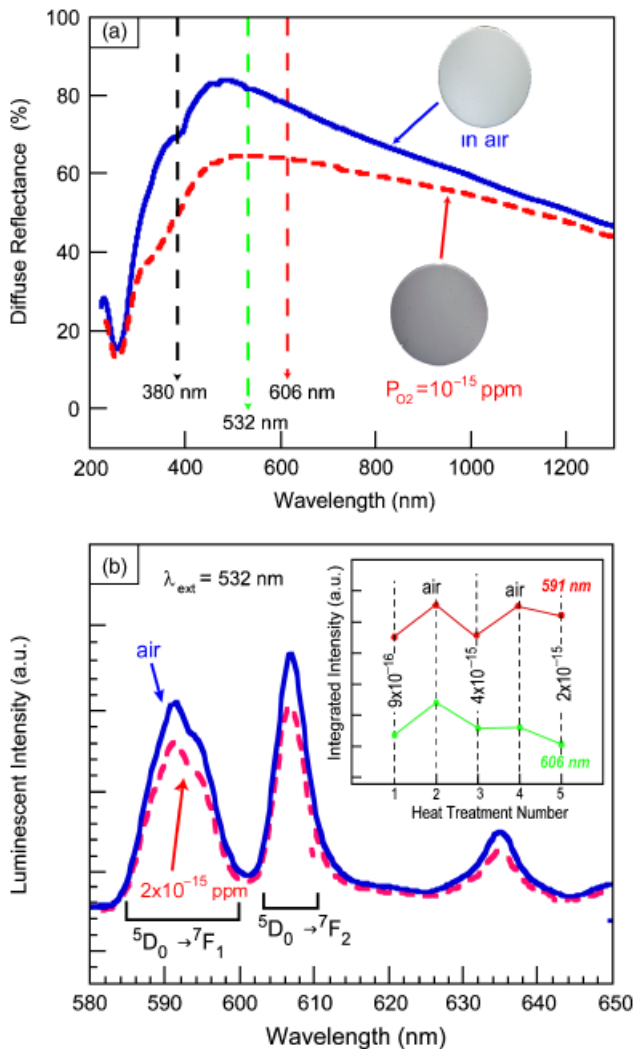
Fig. 3. Luminescence spectra of the 1 a/o Eu^{3+}-doped 8YSZ sensor layer in air with increasing temperatures. The three principal peaks correspond, with increasing wavelength, to the $^5D_0-^7F_1$, the $^5D_0-^7F_2$ and $^5D_1-^7F_2$ transitions. The peak labeled with a star is the laser leakage through the filter. It is used to normalize the luminescence spectra. YSZ, yttrium-stabilized zirconia.

the luminescence spectra of the sensor layer collected in air at successively higher temperatures. The luminescent intensity of the peak at 606 nm decreased exponentially with increasing temperature and was overwhelmed by the background noise above 700°C, as can be seen more clearly in Fig. 4(a). Superim-

Fig. 2. (a) Diffuse reflectance spectra and micrographs of the sample after annealing in air (solid blue lines) and at $P_{O_2} = 2.3 \times 10^{-15}$ ppm (red dash lines). Also indicated are the position of the excitation wavelength (532 nm) and the emission wavelength used for temperature measurement (606 nm). (b) Luminescent spectra of the sample before and after reducing heat treatments. The electronic transitions corresponding to each emission peak were also indicated in (b). The evidences of recovery of the luminescent intensity under the peaks of 591 and 606 nm after the alternating heat treatments in reduced atmospheres and air are shown in the inset. The unit of oxygen partial pressure is ppm in the inset.

beginning at 800 nm and continuing down to almost the band edge, has previously been reported in cubic YSZs subject to electro-reduction.[13] The increase in absorption is particularly marked at wavelengths around 380 nm, a feature identified with excitation of charged vacancies. After annealing in air, the white appearance of the coating was restored and the diffuse reflectance returned to the upper curve.

There was no significant change in the Eu^{3+} luminescence spectrum of the coating after being subjected to reducing atmosphere, as shown in Fig. 2(b), except for a small but noticeable decrease in overall intensity. As indicated in the inset of Fig. 2(b), this could also be recovered on annealing in air and, within experimental uncertainty, was reversible upon repeated reduction–oxidation cycles. The luminescent lifetimes, after 532 nm excitation, were measured both in fully oxidized status and after being annealed in reducing atmosphere. As shown, the decrease in luminescent intensity did not influence the lifetime.

(2) High-Temperature Luminescence
The luminescence of the Eu^{3+}-doped 8YSZ sensor layer was firstly collected at high temperatures in air. Shown in Fig. 3 are
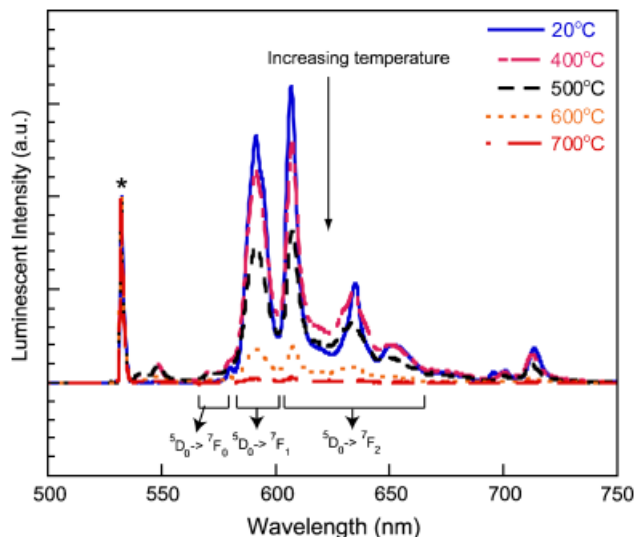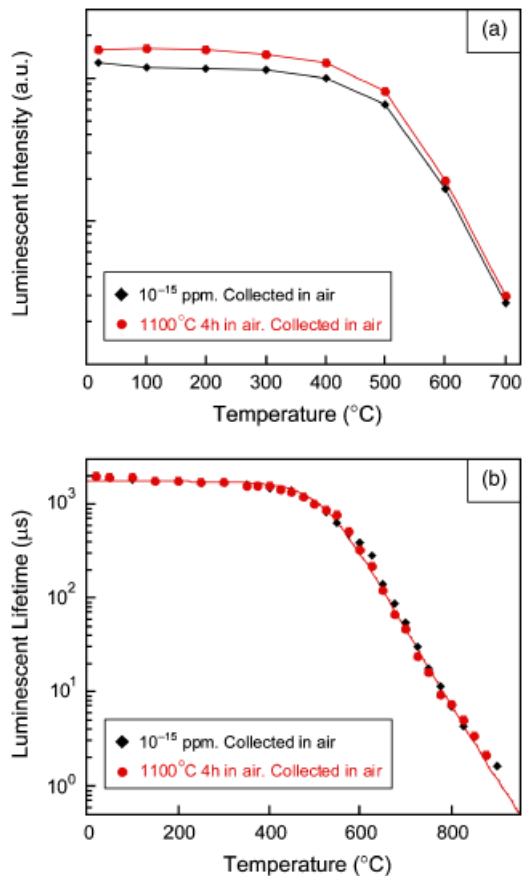

Fig. 4. Measurements in air with the 532 nm excitation. (a) Luminescent intensity under the peak of 606 nm ($^5D_0-^7F_2$) with increasing temperature in air and (b) dependences of luminescent lifetime on temperature, for the fully oxidized coating (●) and after reduction at a partial pressure of 10^{-15} ppm (◆). The line drawn through the lifetime data is the best fit to the charge transfer model.[12]
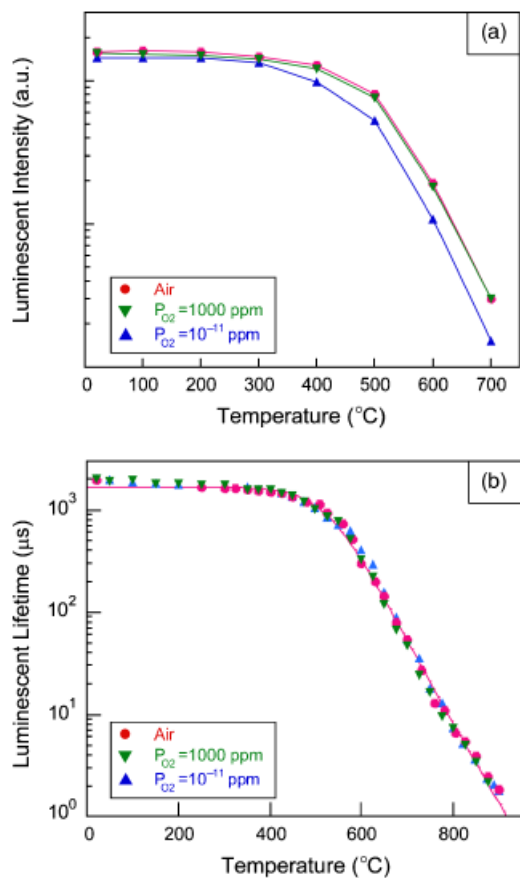
Fig. 5. *In situ* measurements. (a) Luminescent intensity under the peak of 606 nm with increasing temperature and (b) dependences of luminescent lifetime on temperature. Fully oxidized coating collected in air (●), at $P_{O_2} = 1000$ ppm (▼), and at $P_{O_2} = 10^{-11}$ ppm (▲). The line drawn through the lifetime data is the best fit to the charge transfer model.[12]

posed in Fig. 4(a) are the luminescent intensity of the 606 nm peak collected from the sample that had first been reduced at $P_{O_2} = 10^{-15}$ ppm at 1100°C. At room and intermediate temperatures, the luminescent intensity of the partially reduced sample was lower than that of the fully oxidized sample, which is attributed to the increase in optical absorption associated with the reduction process. The differences persist up to about 600°C and became smaller thereafter, suggesting that reoxidization of the coating was occurring during the course of the measurements. (Typically, measurement of the temperature dependence up to 900°C takes about 10 h.) The luminescent lifetimes with increasing temperature were also collected in air, both in fully oxidized and partially reduced state, as shown in Fig. 4(b). The luminescence of the Eu^{3+}-doped 8YSZ sensor layer was then collected *in situ* under a reducing atmospheres of $P_{O_2} = 1000$ and 10^{-11} ppm. The luminescent intensity of the 606 nm peak was slightly lower than that collected in air as shown in Fig. 5(a). The reason for this slight decrease is not clear at this point but could be partially attributed to the increased scattering of the excitation laser pulse from the Argon gas in the chamber compared with the scattering from oxygen and nitrogen. The differences in luminescent intensity became larger at 400°C and persist up to over 700°C until the luminescent signal was again overwhelmed by background noise. As with the measurements made in air, although there was a decrease in the luminescent intensity at higher temperature in the reducing atmospheres, the luminescent lifetime was not influenced, as shown in Fig. 5(b) and no significant change was observed in the lifetime-temperature dependences obtained in either air or in the reducing atmospheres.

IV. Discussion

The major finding of this work is that although the luminescence intensity from Eu^{3+} doping of YSZ decreases when annealed in highly reducing atmospheres, the luminescence lifetime is unaffected and the characteristic dependence of luminescence lifetime on temperature on which luminescence thermometry is based is unchanged from that obtained in air.

The decrease in luminescence intensity is attributed to the increase in optical absorption that occurs as zirconia is reduced.[13] The absorption decreases both the incident excitation intensity as it propagates into the coating and the intensity of the back-scattered light, from porosity within the coating, that can also excite luminescence in the thin sensor layer on top of the coating. Both the excitation wavelength and the luminescence wavelengths are in the wavelength range over which the diffuse optical reflectance is decreased by increased absorption. The reflectance data also suggests that excitation at 355 nm, another wavelength commonly used for luminescence thermometry, would be more adversely affected if YSZ sensor coatings were subject to reducing atmospheres.

The lifetime-temperature dependences were identical over the entire temperature range from room temperature up to ∼900°C, the maximum temperature the measurements could be made. Both the MPR model and the CT model were used to obtain a fit to the luminescent lifetime-temperature dependence. The fitting results were shown in Figs. 4(b) and 5(b). For the MPR model, $\Delta E = 1.48$ eV and $\omega = 600$ R/cm was used, while for CT model, $E_a = 2.07$ eV and $h\nu = 4 \times 10^{-6}$ eV was used to fit the data. Although the two sets of data could be fit equally well with either the MPR model or a CT model up to about 750°C, the fit was superior at the higher temperatures with the CT model.

While the absence of any changes in the luminescence lifetime upon reduction is important for the applications of luminescence thermometry, it is somewhat unexpected because the luminescence lifetime is usually considered to be sensitive to the local atomic environment of the luminescent ion. However, as discussed in the following the insensitivity to reduction is consistent with what is known about the mechanisms responsible for the increased optical absorption in zirconia.[13] Reduction by both heating in highly reducing atmospheres and by passage of high currents ("electro-reduction") is attributed to the formation of color centers, associated with the formation of oxygen vacancies, and, in extreme cases, possibly the formation of zirconium metal colloids.[13] The vacancies formed by reduction are believed to form at random in the crystal structure and are not considered to be associated with the Y^{3+} ions. They are doubly charged and it has been concluded that the darkening results from the excitation of electrons trapped at these vacancies, in essence F centers.[14–16] In contrast, the vacancies associated with the substitution of Y^{3+} ions form defect complexes with the Y^{3+} ions and are believed to be singly occupied vacancies.[17] Furthermore, simulations and EXAFS results suggest that the vacancies formed to charge compensate for the Y^{3+} ions are not nearest neighbors but are preferentially located at the next nearest neighbor sites.[18] Together this prior knowledge suggests that the vacancies introduced by reduction are unlikely to affect the CT mechanism associated with the Y^{3+}–O$_O^X$—Zr^{4+} ligand that controls the luminescence lifetime. This conclusion is also consistent with our previous findings that the luminescence lifetime of Eu^{3+} in YSZ is insensitive to the concentration of Eu^{3+} dopant.[19]

Finally, the other two findings of interest are the reversibility upon repeated reduction–oxidation and the temperature at which reoxidation is complete. Our data indicate that the processes of reduction and oxidation are reversible and that the fully oxidized state can be recovered simply by annealing in air at 1150°C. The recovery of the luminescence as the highly reduced coating was heated in air indicates that the coating was reoxidized by the time it was heated to 600°–700°C (Fig. 4.) Based on the data for the oxygen diffusivity in YSZ,[20] oxygen would diffuse ∼8 μm into a dense coating within 8 h at this

temperature. As the sensor layer is porous, complete reoxidation during the experiment is, thus, quite reasonable.

V. Conclusions

The luminescence from Eu^{3+}-doped 8YSZ is remarkably insensitive to the oxygen partial pressure from ambient down to $\sim 10^{-15}$ ppm. Although the luminescent intensity of the sensor layer decreases due an increase in optical absorption associated with the formation of oxygen vacancies and point defects, the reduction showed no significant effects on the luminescence of the sensor layer at room temperature. Furthermore, the decrease in luminescence intensity could be recovered after annealing again in air at temperatures above $\sim 600°C$. The differences between the lifetime-temperature dependences collected in air and at $P_{O_2} = 10^{-11}$ ppm are well within experimental uncertainties demonstrating that the luminescence lifetime is independent of the oxygen partial pressure, validating the possible use of Eu^{3+}-doped 8YSZ sensor layers even in extremely reducing atmospheres. The insensitivity to the partial pressure of oxygen also suggests that the CT mechanism responsible for thermal quenching is associated with the Y^{3+}–O_O^X—Zr^{4+} ligand and is unaffected by next nearest neighbor vacancies introduced by reduction.

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