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Embedded Optical Sensors for Thermal Barrier Coatings

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Abstract

In the second year of this program on developing embedded optical sensors for thermal barrier coatings, our research has focused three topics: (i) Eu^{3+} doping for temperature sensing, (ii) the effect of long-term, high-temperature aging on the characteristics of the luminescence from the Eu^{3+} ions of 8YSZ materials, (iii) construction of a fiber-optic based luminescence detector system. It has been demonstrated that the variation in luminescence lifetime with temperature is identical for electron-beam evaporated Eu-doped YSZ coatings as for bulk ceramics of the same composition. Experiments indicate that the luminescence lifetime method of measuring temperatures is sensitive up to 1150°C for both Eu-doped YSZ coatings and Eu-doped $\text{Gd}_2\text{Zr}_2\text{O}_7$. Furthermore, the technique is sensitive up to 1250°C for the composition $\text{Eu}_2\text{Zr}_2\text{O}_7$. The luminescence spectra Eu-doped YSZ are insensitive to long-term aging at high-temperatures, even to 195 hours at 1425°C , except for a small frequency shift that is probably too small in measure except with instruments of the highest spectral resolution. The temperature of 1425°C is much higher than present engines attain or even planned in the foreseeable future. Nevertheless, experiments are on-going to explore longer term exposures. A fiber-optic based luminescence system has been constructed in which the hottest section of fiber operates to at least 1250°C .

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1. SENSING WITH EUROPIUM DOPING

Europium doping of both yttria-stabilized zirconia and zirconate pyrochlore based thermal barrier coatings and bulk materials has been studied in detail. Europium is one of the chromophores investigated in the first year and one that can be readily incorporated with the crystal structure of both classes of thermal barrier coatings. Preliminary results of the temperature dependence of Eu^{3+} in $\text{Gd}_2\text{Zr}_2\text{O}_7$ were reported in the first annual report.

The electronic transitions associated with Eu^{3+} ions are shown in figure 1. For reference, the energy corresponding to the band gap absorption of zirconia is indicated together with the energies of the Krypton-Fluoride UV laser and the frequency doubled Nd:YAG pulsed laser used in our work.

Figure 1. The electronic energy levels of Eu^{3+} ions lying within the energy region over which zirconia is transparent, and hence, useful for sensing.

In this report we describe luminescence from both thermal barrier coatings and bulk ceramic samples. The former were deposited by electron-beam deposition at both UCSB and at Howmet Research Corporation. The latter, bulk materials were prepared by the methods described in detail in the first annual report. In addition to Eu^{3+} doped YSZ, a series of zirconate compositions with different Eu^{3+} concentrations lying along the solid solution range between $\text{Gd}_2\text{Zr}_2\text{O}_7$ and $\text{Eu}_2\text{Zr}_2\text{O}_7$, and shown in figure 2, were studied together with Eu^{3+} doped $\text{Sm}_2\text{Zr}_2\text{O}_7$. All these compositions are potential sensor thermal barrier coating materials.

Figure 2. Range of compositions investigated as zirconate thermal barrier coatings represented on the $\text{ZrO}_2\text{-Eu}_2\text{O}_3\text{-Gd}_2\text{O}_3$ (Y_2O_3) ternary phase diagram.

Excitation spectra were recorded for the different Eu^{3+} doped materials using a Perkin-Elmer spectrometer to ascertain the optical wavelengths that can efficiently excite the characteristic Eu^{3+} luminescence. The results are summarized in the excitation spectra superposed in figure 3 below.

Figure 3. Wavelength spectra of Eu-doped YSZ, $\text{Eu}_2\text{Zr}_2\text{O}_7$ and Eu-doped $\text{Sm}_2\text{Zr}_2\text{O}_7$ and $\text{Gd}_2\text{Zr}_2\text{O}_7$ for excitation of the Eu^{3+} luminescence line at 606 nm. The principal electronic levels of the Gd^{3+} and the Eu^{3+} ions are also shown.

The luminescence spectra of Eu^{3+} excited with a frequency-doubled Nd:YAG laser at 532 nm is shown in figure 4 for the same compositions in figure 3.

Figure 4. A portion of the optical luminescence spectra of Eu^{3+} dopants recorded from the indicated compositions excited at 532 nm. The line arrowed, at 606 nm, is used for luminescence decay measurements of temperature.

2. TEMPERATURE SENSING WITH EUROPIUM DOPING

The method we have selected for measuring temperature is from the decay in luminescence intensity as a function of time after exciting the material with a short laser pulse. Two examples are shown in figure 5. The luminescence decay is typically characterized by a bi-exponential decay, such as shown for one of the Eu-doped $\text{Gd}_2\text{Zr}_2\text{O}_7$ at 600°C , consisting of a very short decay followed by a longer decay. In some materials, such as that shown for the $(\text{Eu}_{0.5}\text{Sm}_{0.5})_2\text{Zr}_2\text{O}_7$ decay at 500°C , the very short decay is masked by the intensity of the longer decay. The longer decay is consistently used as a measure of temperature.

Figure 5. Two examples of the decays in luminescence intensity of the 606 nm Eu^{3+} line after the excitation laser pulse has been turned off.

The variation in decay with temperature for all the materials investigated exhibited two characteristic regimes as illustrated in figure 6. At low and intermediate temperatures, the luminescence lifetime is independent of temperature whereas at higher temperatures, the lifetime decreases exponentially with increasing temperature. The high temperature regime is of primary interest for measuring thermal barrier coating temperatures.

Figure 6. The temperature dependence of the luminescence lifetime for Eu-doped YSZ and Eu-doped $Gd_2Zr_2O_7$. The two curves shown for the Eu-doped $Gd_2Zr_2O_7$ material correspond to the fast and slow decays mentioned in the text. The most notable feature of the data is that, within experimental uncertainty, the slow lifetimes are the same for the two materials.

The striking and surprising feature of the data is that the lifetime-temperature curves of both the Eu-doped YSZ and the Eu-doped $Gd_2Zr_2O_7$ materials are the same at high temperatures. This finding seems to be related to the similarity in the local atomic arrangement around the Eu^{3+} ion in the crystal structure of the two materials. The origin of this unexpected result is presently being investigated.

One of the most important findings we have made is that the lifetime-temperature curves are the same for both bulk material and coatings deposited by electron-beam evaporation. Figure 7 shows a comparison of the curves for a 10 micron thick Eu-doped YSZ sensor coating, deposited on a standard YSZ coating, and a bulk ceramic pellet of the same composition. Although, as expected, there is a substantial difference in luminescence intensity, the lifetimes are the same up to the maximum temperature (1100°C) to which we could record reasonable spectra.

Figure 7. Comparison of the luminescence lifetime decays for a 10 micron thick coating, deposited by electron beam evaporation and a bulk ceramic pellet. The composition of the two materials was 1m/o $\text{EuO}_{1.5}$ in standard 8YSZ.

A series of experiments have also been performed on other zirconate pyrochlores, in which the A-site tri-valent cation (the Gd in $\text{Gd}_2\text{Zr}_2\text{O}_7$) is partially, or completely, replaced by other tri-valent ions, such as Eu^{3+} . The composition that exhibits measurable luminescence to the highest temperature was found to be europium zirconate, $\text{Eu}_2\text{Zr}_2\text{O}_7$. As shown in figure 8, where the data is compared with that of the Eu-doped YSZ, the lifetimes are longer and can be measured out to about 1280°C. This maximum temperature appears to be currently limited by our photomultiplier tube rather than by the material itself suggesting that even higher temperatures should be measurable.

Figure 8. Comparison of the luminescence lifetime for Eu-doped 8YSZ and the europium zirconate, $\text{Eu}_2\text{Zr}_2\text{O}_7$. With our current measurement system, described in section 4 below, temperatures up to 1280°C have been measured.

3. LONG TERM, HIGH TEMPERATURE STABILITY

Current thermal barrier coatings, whether deposited by electron beam evaporation or plasma-spraying, are yttria-stabilized zirconia and comprise the metastable tetragonal-prime structure. After extended exposure at very high-temperatures, this metastable phase is known to evolve to a mixture of the tetragonal and cubic phases. On subsequent cooling, the tetragonal phase can transform to the monoclinic phase. This transformation, which is rarely seen in any service parts, is considered undesirable since it can be accompanied by microcracking and degradation of the coating. To address the question as to whether long-term, high temperature exposure affects the luminescence spectra and lifetimes, electron-beam evaporated coatings of Eu-doped YSZ have been aged for different lengths of time at 1425°C and subsequently aged to produce different concentrations of monoclinic zirconia.

3.1. Aging Treatment

The samples were aged in air for different lengths of time at 1425°C . This temperature was chosen as it has been used in an earlier study of the phase transformation behavior of YSZ coatings by Raman spectroscopy and X-ray diffraction enabling a direct comparison with the luminescence observations being made in this investigation. As previously reported, phase separation evolution occurs but no transformation to monoclinic occurred even after 195 hours at 1425°C . To produce materials with different concentrations of monoclinic phase, the samples heated for different lengths of time at 1425°C were subsequently aged at 150°C in air for 185 hours. The volume fraction of the monoclinic phase was determined by Raman spectroscopy.

3.2. Effect of Aging on Luminescence

Prolonged annealing at 1425°C in air did not have any detectable effect on the luminescence spectrum from either the Eu^{3+} ions in the coatings or from the Er^{3+} ions, which were present as an impurity. Upon subsequent low-temperature aging at 150°C, the spectra remained qualitatively the same (figure 9) even after 49% of the coating had transformed from tetragonal to monoclinic zirconia.

Figure 9. The characteristic luminescence lines of Eu^{3+} from (i) as-deposited EB-PVD coating, (ii) the same coating after annealing for 195 hours at 1425°C, and (iii) after subsequent aging at 150°C for 185 hours, an aging treatment that transforms 49% of the coating to monoclinic zirconia. The luminescence line at 606 nm, used for temperature sensing and arrowed, is unaffected by this aging treatment.

Detailed spectral analysis revealed a small, linear shift in the frequency of the 606 nm luminescence line (figure 10).

Figure 10. Systematic shift in the position of the 606 nm peak with increasing concentration of monoclinic phase in a Eu-doped YSZ coating, deposited by electron beam evaporation, and aged to give the indicated monoclinic phase concentrations.

Measurements of the luminescence lifetime at room temperature indicated that the transformation does not alter the bi-exponential decay and there are no additional features in the spectral decay. There is some variation in the lifetime with transformation to the monoclinic phase (table I) but this is within the uncertainty typically seen for room temperature lifetime measurements. Experiments are underway to determine if there is any variation at high temperatures, where the sensors would be used.

Figure 11. Luminescence lifetime decays at room temperature with high temperature and intermediate temperature aging, corresponding to the different monoclinic concentrations indicated.

Table I.

Effect of Monoclinic Concentration of Room Temperature Luminescence Lifetime

Monoclinic Phase Concentration (%)	Lifetime (milli-seconds)
0.0	1.60
13.0	1.35
49.0	1.37

4. FIBER OPTIC BASED LUMINESCENCE DETECTOR SYSTEM

During the past year, progress has been made in designing and constructing a portable sensor detector system based on fiber-optic components. The system is shown schematically in figure 12 as implemented in for measurements within a furnace. The same arrangement has also been used to measure luminescence in conjunction with localized surface heating with a CO₂ laser at NASA Glenn. The excitation from a laser, usually a solid-state Nd:YAG laser, is directed onto the coating or bulk sample situated within the furnace and the luminescence collected with a sapphire fiber whose end is positioned close (within a few centimeters) to the sample. The sapphire fiber is coupled to a standard optical fiber, with an in-line filter to remove the laser line, and directly into a photomultiplier tube (PMT) or an optical spectrometer, depending on the luminescence characterization being performed.

For recording the luminescence spectra, the fiber optic is connected to a wavelength dispersive Ocean Optics spectrometer and its output taken straight into a laptop computer for display and recording of the spectra. (In contrast to conventional wavelength spectrometers, the Ocean Optics model has no moving parts). For lifetime measurements, the photomultiplier output is connected to an oscilloscope through a trans-impedance amplifier and the output recorded as a function of time following the trigger pulse sent to trigger the Q-switch of the pulse laser. The oscilloscope output is read directly into a laptop through a GPIB board all under control of LabviewTM software.

In some system configurations, the sapphire fiber has been replaced with a fused silica fiber and the notch filter replaced with a monochromator.

Currently, the largest component of the system, apart from the furnace, is the laser. In the coming year, the use of a GaN diode in place of the laser will be explored.

Figure 12. Schematic diagram of the experimental arrangement used to measure the luminescence lifetime of coatings and bulk materials.

5. PLASMA-SPRAYED COATINGS

Towards the end of the year, we were finally able to obtain Eu-doped plasma-sprayed coatings for investigation. The coatings were a Eu-doped pyrochlore zirconate having a nominal composition of $(\text{La}_{0.5}\text{Eu}_{0.5})_2\text{Zr}_2\text{O}_7$. The coating exhibits strong room temperature luminescence characteristic of Eu^{3+} ion in the pyrochlore structure as shown in figure 13. Although the composition probably contains too high a concentration of Eu^{3+} for use as a sensor to the very highest temperatures, the intense luminescence demonstrates unequivocally that the plasma-spraying process does not destroy the luminescence opening up the possibility of luminescence sensing in plasma-sprayed coatings. Characterization of the temperature dependence of the luminescence decay characteristics is currently underway.

Figure 13. Luminescence from Eu^{3+} ions from a plasma-sprayed $(\text{La}_{0.5}\text{Eu}_{0.5})_2\text{Zr}_2\text{O}_7$ coating excited with 532 nm laser.

FUTURE PLANS

Now that we have demonstrated that the luminescence spectra are unchanged after prolonged high temperature exposure and even conversion to half of the coatings to the monoclinic phase (both more extreme than current coatings are subject to) the focus of the research in the coming year will be on (i) the demonstration of an LED based optic-fiber luminescence detector system, (ii) investigation of the effect of aging on the variation in luminescence lifetime with temperature, and (iii) investigation of plasma-sprayed coatings under combustor-type environments.