

# Non-contact sensing of TBC/BC interface temperature in a thermal gradient

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## Abstract

Luminescence lifetimes of rare-earth ions in yttria-stabilized zirconia have been shown to exhibit temperature sensitivity from 500–1150 °C [Gentleman, M.M. and Clarke, D.R. (2005) *Surface and Coatings Technology* 200, 1264; Gentleman, M.M. and Clarke, D.R. (2004) *Surface and Coatings Technology* 188–189, 93.]. These doped zirconias can be deposited along with standard thermal barrier coatings to create thin temperature sensing layers within the coating. Of particular interest is the temperature at the coating/bond coat interface as the oxidation life of a TBC system is exponentially dependent on this temperature. In this study, thin ( $\sim 10 \mu\text{m}$ ) layers of europia-doped yttria-stabilized zirconia were deposited by EB-PVD onto bond-coated CMSX-4 superalloy buttons to achieve sensor layers located next to the TBC/BC interface. These coatings were then used to measure the interface temperature in a thermal gradient. Combined with pyrometric measurements of the coating-surface temperature and metal-surface temperature, the thermal conductivity of the coating (1.5 W/mK) and heat flux ( $\sim 1 \text{ MW/m}^2$ ) in the tests were calculated.

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## 1. Introduction

The continuing use of, and growing reliance on, ceramic coatings for thermal insulation of hot metallic components in power generation and aerospace turbines has led to the requirement that coatings must not fail during the scheduled lifetime of the component. As a result, a significant effort has been placed on the ability to assess the “health” of these parts during service. Of particular interest is the capability to monitor the temperature of the coating in contact with a blade or vane. This requires a non-contact technique that has the ability to see through the radiation emitted by engine surfaces and the hot gas as well as take a measurement on a moving engine part. Luminescence decay lifetime of a phosphor embedded in the coating is one technique that shows promise to fulfill all these requirements. The use of phosphors to measure temperatures dates back to the work of Bradley [3] and has been reviewed in detail by Allison et al. [4]. More recently the concept has been shown to be applicable to TBC materials and coatings [1,2,5,6]. A funda-

mental requirement of any sensor is that the luminescent phosphor is thermodynamically stable as well as having temperature dependent luminescence lifetime decay.

Thermodynamic compatibility poses a very severe constraint on the possible luminescent phosphors that can be used in thermal barrier coatings because the temperatures are so high and the service life is so long. The phosphor must not only be compatible with the coating material but also the materials in contact with the coating itself. For current coating materials, such as yttria-stabilized zirconia and the zirconates, phase compatibility precludes the use of many well known phosphor hosts such as  $\text{Y}_2\text{O}_3$ , the oxysulphides and  $\text{Y}_3\text{Al}_5\text{O}_{12}$  in thermal barrier systems [2]. For this reason, the use of the coating material itself as the host material is the obvious choice for creating a durable coating that also has sensing capabilities. Crystal chemistry considerations dictate that the luminescent ions must be one or more of the lanthanide ions. The optical properties of these ions further narrows the choice for particular sensor applications.

Previous work has illustrated the ability to measuring temperature using the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition of Eu-doped thermal barrier materials for temperatures ranging from 500 to 1200 °C

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[1]. The luminescence decay times of these materials at high temperatures are sufficiently short that the measurements can be made at speeds considerably faster than the rotational speed of gas turbines. Additionally, in previous work, thermal barrier coatings with rare-earth doped layers were deposited by electron-beam physical vapor deposition (EB-PVD) and the luminescence was excited through undoped zirconia and zirconate coatings with several laser frequencies [2].

In this work, we use the sensor technique to make non-contact measurements of temperature from thin sensor layers located between a superalloy and a standard YSZ coating. These coatings were exposed to a thermal gradient to demonstrate the ability to collect luminescence from a buried layer in the presence of a thermal gradient, and to determine the temperature of the interface. Continuity of heat flux further allows us to calculate the thermal conductivity of the coating from this value providing a direct determination of the thermal conductivity of the coating. These measurements are a vital component in the integration of sensor layers into commercial turbine coatings for health monitoring.

## 2. Experimental details

### 2.1. Sample preparation

The coatings were prepared by electron beam evaporation. The ingot for EB-PVD of the sensor layers was prepared by infiltration of a standard 7YSZ ingot with aqueous  $\text{Eu}(\text{NO}_3)_3$ . The nitrate solution was gelled into the pores of the ingot with  $\text{NH}_4\text{OH}$  and calcined at  $950\text{ }^\circ\text{C}$  to yield a composition of  $\text{Y}_{0.06}\text{Eu}_{0.01}\text{Zr}_{0.93}\text{O}_{1.965}$ . The layered structure was achieved in a single run of EB-PVD by layering the doped ingot with a standard undoped 7YSZ ingot. The final coating consisted of two layers, a Eu-doped layer approximately  $10\text{ }\mu\text{m}$  in thickness at the base of the coating, and an undoped layer on top approximately  $140\text{--}170\text{ }\mu\text{m}$  thick (Fig. 1). The coatings were deposited on CMSX-4, 2.54 cm (1 in.) diameter, 3 mm thick buttons with MDC-150L bond coats.

For comparison, bulk ceramic materials were fabricated via reverse co-precipitation of aqueous  $\text{Eu}(\text{NO}_3)_3$ ,  $\text{Y}(\text{NO}_3)_3$ , and zirconium acetate solutions to achieve the same composition as

the sensor ingot. Following precipitation, the powder was dried, calcined at  $950\text{ }^\circ\text{C}$ , pressed into a pellet, and sintered at  $1200\text{ }^\circ\text{C}$  for 2 h. Raman spectroscopy of the bulk material was used to confirm that they had the tetragonal-prime crystal structure found in coated materials.

### 2.2. Luminescence lifetime calibrations

On the basis of our previous work [1], the luminescence emission spectra were excited using a frequency doubled, Q-switched, YAG:Nd laser emitting at 532 nm and having a pulse length of  $\sim 10\text{ ns}$ . To develop the calibration curves relating luminescence lifetime-decay to temperature, luminescence measurements were first recorded under isothermal conditions inside a box furnace with a thermocouple placed next to coatings and bulk samples to record temperatures. The box furnace was fitted with two optical ports, one for the free-space propagation of laser light into the furnace, and the second for the collection of luminescence via a sapphire light pipe. The light from the sapphire light pipe was then passed through standard fiber optic cable to a laser cut-off filter and luminescence bandpass filter to isolate the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition (at 606 nm) before reaching a Hamamatsu photosensor module. The luminescence intensity was recorded as a function of time after the laser pulse was triggered for an average of 1000 laser pulses in a digital oscilloscope (LeCroy 9310AM). Isothermal measurements of luminescence intensity as a function of time were taken for temperatures between room temperature and the detectability limit of the collection electronics (approximately  $0.01\text{ }\mu\text{s}$  decay time).

### 2.3. Luminescence lifetime measurements in a thermal gradient

Several coatings were subject to high heat flux exposure at NASA Glenn Research Center and luminescence lifetime measurements made under different heat flux conditions. In the NASA rig, a 3.0-kW  $\text{CO}_2$  laser ( $10.6\text{ }\mu\text{m}$  wavelength) is used to heat the outer surface of the coating and the back of the superalloy cooled with a high-pressure compressed air jet (Fig. 2). This generates a heat flux through the coating and the underlying superalloy. The instrumental details of the high heat flux laser rig have been described elsewhere [7]. The temperature at the top

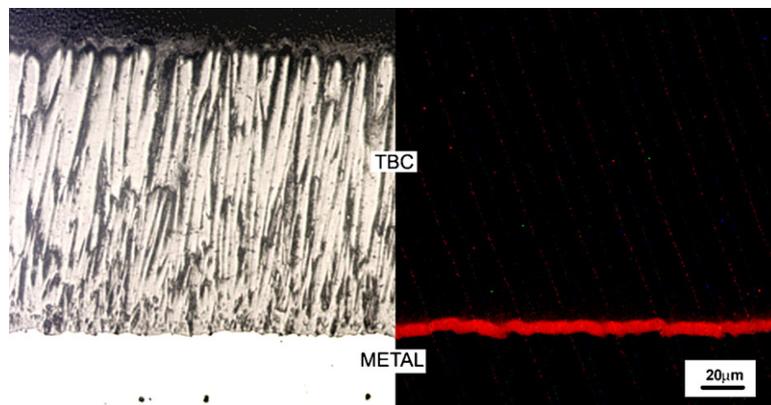


Fig. 1. Optical image of the cross-section of a thermal barrier coating illustrating the location of YSZ:Eu sensor layer appearing bright between the Superalloy and YSZ coating. The left image is a white light image of the coating and the right is the luminescence image from the Eu-layer obtained with UV excitation of the same region.

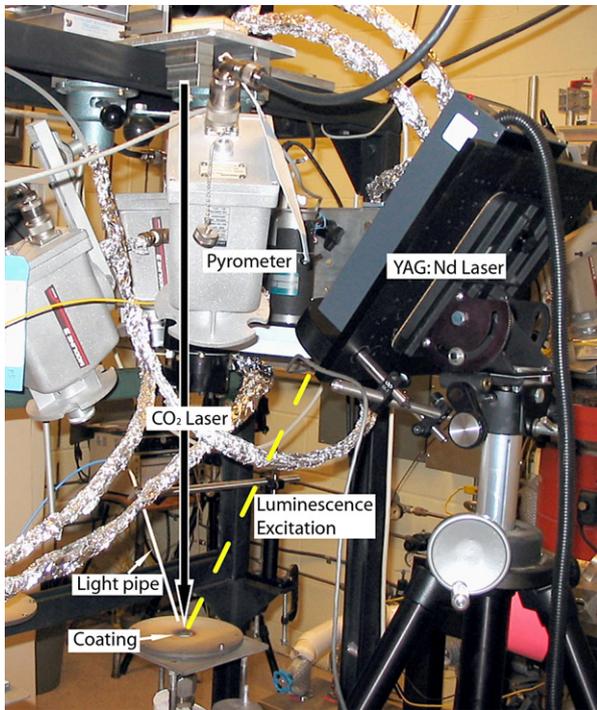


Fig. 2. Photograph of the experimental setup used to measure the temperature at the TBC/BC interface by luminescence while under a thermal gradient at the NASA high heat flux laser rig. The principal components are labeled.

surface of the coating was monitored using an 8- $\mu\text{m}$  infrared pyrometer while a two-color pyrometer was used to monitor the temperature of the metal surface. The  $\text{CO}_2$  laser was used to deliver a constant power of 1060 W to the top surface of the coating and by adjusting the compressed air flow, the metal temperature, the top surface temperature and the heat flux could be varied.

To interrogate the sensor layer while the sample was exposed to the thermal gradient, a solid-state frequency doubled YAG:Nd

laser emitting at 532 nm was directed to illuminate the center of the coating surface while mounted in the high heat flux rig. As in the isothermal furnace tests, the end of a sapphire light pipe was positioned to collect the excited luminescence signal and the luminescence intensity recorded and averaged in the same way as described in the previous subsection. The one difference was that for safety reasons the measurements were made remotely under computer control.

### 3. Results

Before presenting the principal results of this work, which are the measurements of the temperature of the thermal barrier coating in direct contact with the bond-coat, we present our calibration data. As described in the previous section, the calibration curves of luminescence lifetime as a function of temperature were determined for both bulk ceramic samples and coatings. Both forms of the sensor material exhibited double exponential decays over the entire temperature range and were therefore fitted using the function:

$$A = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (1)$$

where  $A$  is the intensity and  $\tau$  the luminescence lifetime for the individual decays (Fig. 3). The second, longer luminescence lifetime ( $\tau_2$ ) was used for calibration purposes and its value is shown as a function of temperature for both the bulk and coatings in Fig. 4. The second, longer decay was chosen for its length, which allowed measurement to higher temperatures than for the shorter decay, and for the reason that it was not dependent on the excitation intensity. The luminescence lifetime data was consistent with a temperature dependent multiphonon relaxation model [8]:

$$w_{total} = w_r + w_{mp}(0)(n + 1)^p \quad (2)$$

where  $w_r$  is the rate of radiative emission,  $w_{mp}(0)$  is the rate of multiphonon emission at 0 K, and  $n = [\exp(h\nu/kT) - 1]^{-1}$  is the phonon population density,  $\nu$  is the frequency of the phonon,

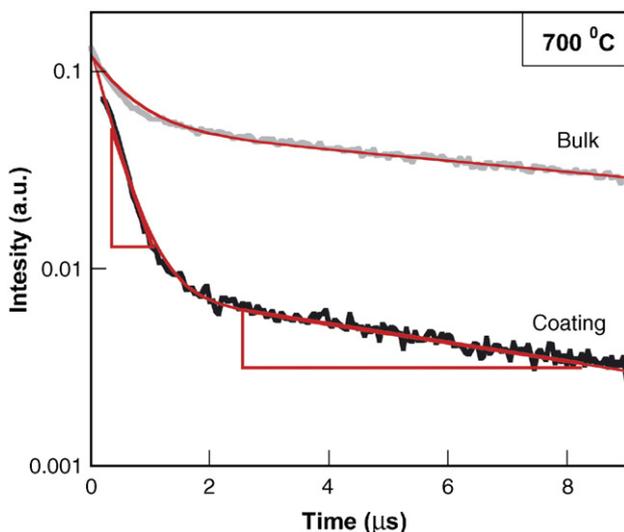


Fig. 3. Representative luminescence lifetime decays for the bulk and coated samples at 700 °C. While the long decays have the same slope, the faster decay varies in the two materials. The longer decay is used for temperature measurement.

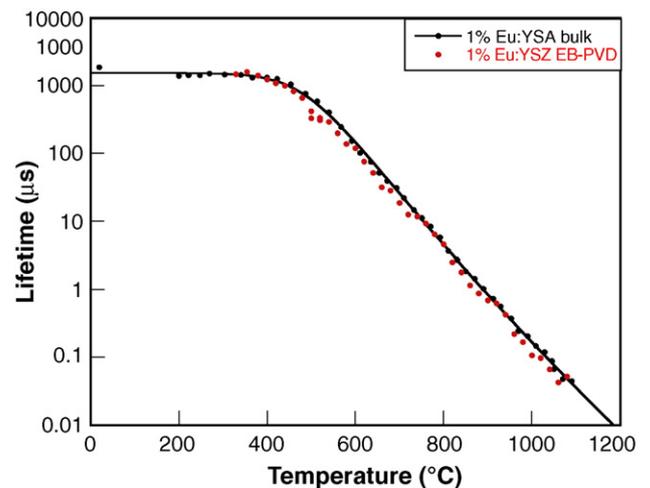


Fig. 4. Comparison of the luminescence lifetime decays as a function of temperature for the bulk and coated materials. The decays are fit using a multiphonon relaxation model, Eq. (3) in the text.

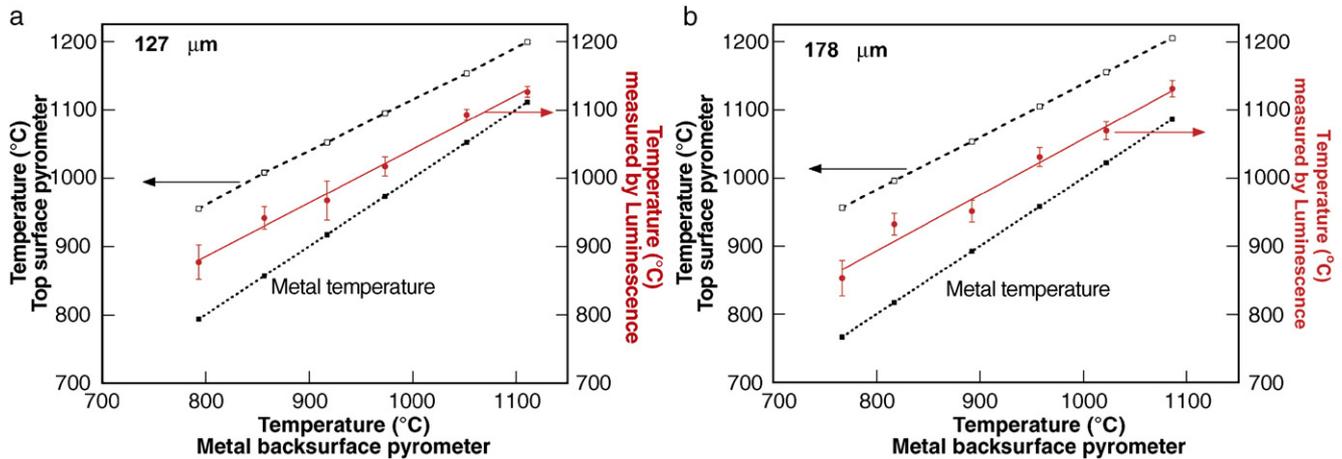


Fig. 5. Temperatures measured at the top of the TBC and bottom surface of the CMSX4 alloy by pyrometry and the TBC/BC interface temperature by luminescence for two different coatings. (a) 127  $\mu\text{m}$  and (b) 178  $\mu\text{m}$  thick coatings.

and  $p$  is the number of phonons required to bridge the energy gap corresponding to the energy of the emitted luminescence,  $16,500\text{ cm}^{-1}$ . The phonon energy was taken to be that of the highest energy Raman band for tetragonal YSZ. Its energy and temperature dependence have been determined recently [9] and this information was used in fitting the calibration data. The fitting of the data to the multiphonon model was then used to represent the calibration curve in converting lifetime measurements made under the thermal gradient tests to temperature of the TBC/BC interface temperature.

Two examples of our temperature measurements are shown in Fig. 5 for a variety of heat flux conditions produced by changing the cooling rate on the back of the superalloy. One plot is for a coating that is 127  $\mu\text{m}$  thick and the other for a 178- $\mu\text{m}$  thick coating. In both cases, the sensor layer is 10  $\mu\text{m}$  thick. In these plots, the pyrometric measurements of the top surface of the coating and the luminescence measurements are both plotted as a function of the pyrometric measurements of the alloy surface temperature.

In addition to the measurements of the TBC/BC temperature, the steady state, one-dimensional heat flow in the NASA rig, enabled the thermal conductivity of the coating,  $\kappa_{\text{TBC}}$  to be determined. Assuming one-dimensional heat flow, the heat flux,  $q$ , through the coating and the superalloy are the same:

$$q = \kappa_{\text{TBC}} \frac{\Delta T_{\text{TBC}}}{h_{\text{TBC}}} = \kappa_{\text{alloy}} \frac{\Delta T_{\text{alloy}}}{h_{\text{alloy}}} \quad (3)$$

$\Delta T$  is the temperature drop across either the coating or alloy,  $\kappa$  is the thermal conductivity of the layer, and  $h$  is the thickness of the layer. Using the temperature measurement of luminescence at the interface and the pyrometry measurements of the top and bottom surfaces, both the temperature drop across the coating and metal were determined. Using the reported temperature dependence of the thermal conductivity of CMSX-4 alloy [10], the thermal conductivity of the coating was calculated to be 1.5 W/mK over the range of 850 to 1150  $^{\circ}\text{C}$ . The corresponding heat fluxes were determined from Eq. (3). These ranged from 0.4 to 1 MW/m<sup>2</sup>.

#### 4. Discussion

The principal finding of our work is that luminescence of a Eu-doped YSZ sensor layer buried under a standard YSZ coating can be used to measure the temperature at the TBC/BC interface in the presence of a thermal gradient under typical thermal gradients and temperatures of coatings in engines today. These results demonstrate that the luminescence lifetime method of measuring temperature can be implemented using europium ions incorporated within the crystal structure of current EB-PVD thermal barrier coatings and the temperature measurement can be localized by controlling the deposition process. The fact that the luminescence was localized to the TBC/BC interface was confirmed by observations of the cross-section of one of the coatings after the thermal gradient measurements. This is illustrated in Fig. 1 which is a superposition of a normal optical micrograph, to reveal the coating and the alloy, and a luminescence image recorded using the luminescence from the Eu-ions. There is also no apparent diffusion of the  $\text{Eu}^{3+}$  ions into the rest of the coating after either the isothermal treatments or cycling in the high heat flux rig. This verifies that the temperatures measured by the luminescence lifetime-decay technique provide us with the temperature of the TBC/BC interface and not from some other depth of the coating. This is vitally important since the technique is an average of the luminescence from all ions excited. If the ions had been distributed at different depths then the luminescence lifetime would have been a convolution of the lifetimes at different depths within the thermal gradient. In principal, this can be detected as the luminescence decay would have been a “stretched” exponential rather than a pure exponential. This, and other higher magnification micrographs, also illustrates that there is no discontinuity in the coating caused by the switch from the Eu-doping to the undoped ingot during deposition. The presence of uninterrupted single crystal columns suggests that the addition of the sensor layer did not disturb the integrity of the coating and should not decrease the life of the coating.

Our current detection system limits us to measurements of interface temperatures of about 1150  $^{\circ}\text{C}$ . With more efficient

collection optics and detectors as well as higher speed electronics, higher interface temperatures can be measured allowing the technique and the Eu-doped coatings to be used to still higher temperatures. The fitting to the multiphonon model indicates that increasing the detection limit by only a factor of ten would enable us to measure temperatures as high as 1250 °C. The other attribute of the Eu-doped coatings is that the luminescence lifetime is sufficiently short that the technique has the potential for measuring the temperature of rotating blades and other components [1].

The lifetime data presented also shows several interesting features apparently peculiar to the  $\text{Eu}^{3+}$  luminescence in yttria-stabilized zirconia. First, the luminescence lifetime of the second, longer exponential decay,  $\tau_2$ , is the same for both the bulk and coated materials over the temperature range explored up to 1150 °C. Rare-earth ion luminescence is known to have very little sensitivity to the host material because the optically active  $4f$  electrons of the ions are shielded by the outer  $5s$  and  $5d$  shells [11]. This shielding may also create an insensitivity of the luminescence lifetime in the slightly different environments of the bulk and coated material. By contrast, the fast decay,  $\tau_1$ , which is usually attributed to luminescence quenching by energy transfer to defects, shows sensitivity to the changes in local environment from bulk to coated material [12]. Specifically, in the coating, the intensity of the fast decay is higher with respect to the second and has a lifetime that is approximately 25% faster than that seen in the bulk. The origin of this difference is not known but may be related to the presence of the fine porosity within the coatings. As mentioned earlier, the temperature dependence is attributed to non-radiative transitions associated with the excitation of lattice phonons. In this mechanism, the energy of the excited state, instead of being radiated as a detectable photon, excites phonons through an ion–phonon coupling mode. The simplest model ascribes this to phonons of all the same energy and assumes that this is the highest energy phonon. In the case of YSZ, the  $\text{B}_{1g}$  phonon mode, with room temperature energy of  $648 \text{ cm}^{-1}$  determined from Raman

spectroscopy is likely to be the primary phonon mode responsible for the multiphonon relaxation. Using the measured temperature dependence of the Raman spectra, between 25 and 27 phonons are required for the non-radiative transition over the temperature range examined. Although the energy of the  $\text{B}_{1g}$  mode provides a good fit of the data for the dilute concentrations of  $\text{Eu}^{3+}$  used in the sensors described in this work more work is needed to determine if they are appropriate for other, higher dopant concentrations. Nevertheless, the fact that all the lifetime data fits the multiphonon relaxation model suggests that the Raman spectra provide a valuable guide to selecting other combinations of luminescent ions and coating materials for future high-temperature thermometry.

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### References

- [1] M.M. Gentleman, D.R. Clarke, Surf. Coat. Technol. 200 (2005) 1264.
- [2] M.M. Gentleman, D.R. Clarke, Surf. Coat. Technol. 188–189 (2004) 93.
- [3] L.C. Bradley, Rev. Sci. Instrum. 24 (1953) 219.
- [4] S.W. Allison, L.A. Boatner, G.T. Gillies, Appl. Opt. 34 (1995) 5624.
- [5] S. Allison, G. Gillies, Rev. Sci. Instrum. 68 (1988) 2615.
- [6] J.P. Feist, A.L. Heyes, J.R. Nicholls, Proc. Inst. Mech. Eng. 215 (2001) 333.
- [7] D.M. Zhu, R.A. Miller, J. Therm. Spray Technol. 9 (2000) 175.
- [8] H.W. Moos, J. Lumin. 1 (1970) 106.
- [9] M.M. Gentleman, V. Lughii, J.A. Nychka, D.R. Clarke, Int. J. Appl. Ceram. Technol. 3 (2006) 105.
- [10] “CMSX Property Data,” Cannon-Mudkegon Corporation, Muskegon, MI, 1994.
- [11] B. Henderson, G.F. Imbusch, Oxford University Press, New York, 1989.
- [12] F. Kallendonk, G. Blasse, J. Chem. Phys. 75 (1981) 561.