Irreversible Phase Transitions due to Laser-Based T-Jump Heating of Precursor Eu:ZrO₂/Tb:Y₂O₃ Core/Shell Nanoparticles

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Abstract

Amorphous precursors of Eu-doped-ZrO₂/Tb-doped-Y₂O₃ (p-Eu:ZrO₂/p-Tb:Y₂O₃) core/shell nanoparticles are rapidly heated to temperatures between 200 °C and 950 °C for periods between 2 s and 60 s using a CO₂ laser. During this heating process the nanoparticles undergo irreversible phase changes. The fluorescence spectra due to Eu³⁺ dopants in the core and Tb³⁺ dopants in the shell are used to identify distinct phases within the material and to generate time/temperature phase diagrams. Such phase diagrams can potentially help to determine unknown time/temperature histories in thermosensor applications.

Keywords

Irreversible phase changes; core/shell nanoparticles; luminescent probes; T-jump

Graphical abstract

A CO₂ laser is used for rapid heating of p-Eu:ZrO₂/p-Tb:Y₂O₃ core/shell nanoparticles. Optical spectra are used to identify distinct phases and to determine its thermal history.

1. Introduction

Understanding and controlling phase changes in materials is of fundamental importance for a variety of applications. As more and more applications use and rely on nanophase materials, it is important to develop a better understanding of phase changes in these materials.¹⁻⁵ The time-dependence of phase changes in nanometer-sized materials is different than it is in bulk materials. For example, solid-solid phase transitions in bulk materials are thought to originate at grain boundaries, where the bulk breaks up into grains, which then start to undergo a phase transition. The transformation from one bulk phase to another bulk phase requires that all the grains change phase, which limits the time of how fast a phase transition can occur. Nanometer-sized materials are too small for grain boundaries, and phase changes originate from single nucleation events in a coherent manner, leading to a much faster response.⁶ Also, nanosize materials can exhibit phases that are not stable in bulk materials under ambient conditions. For example, the monoclinic phase has been observed in nanosize Eu_2O_3 and is stable under ambient conditions.⁷ High pressure is required to prepare this phase in the bulk.

Nanometer-sized particles are often synthesized via wet-chemical techniques that result in the formation of salt precursors such as carbonates or hydroxides. Calcination is required to convert these precursors from the amorphous salt phase to a crystalline oxide phase. During this process, the material undergoes several distinct changes such as thermal decomposition, nucleation, and growth of the crystalline phase. Exactly how the different phases in the nanometer-sized materials form and under what conditions they undergo phase transitions is not well understood. The transitions are expected to

depend on a variety of variables and parameters, including the synthesis technique, the size of the initial particles, the level and type of agglomeration, absolute temperatures and pressures, as well as their rate of change.

Numerous reports have demonstrated the suitability of using optically active rare earth (RE) dopants to probe the phases of nanophase oxides and oxide precursors.⁷⁻¹⁰ These RE ions probe the local structural environment, which determines the optical properties such as fluorescence, excitation, fluorescence-linewidth, fluorescence lifetime, and energy-transfer between dopant ions. A change in ambient conditions, such as pressure changes and/or temperature changes, will lead to structural changes in the material which can be detected by measuring changes in the optical properties.

We have previously applied the use of RE ions to probe fast temperature-induced phase changes in nanopowders of oxide precursors and to correlate these irreversible phase changes with the heating temperature.¹¹⁻¹⁷ We used wet-synthesis techniques to prepare precursors of Y_2O_3 (p- Y_2O_3), ZrO_2 (p- ZrO_2), and La_2O_3 (p- La_2O_3) with well-defined spherical shapes, and we also demonstrated the synthesis of core/shell nanoparticles using different oxide precursors (e.g. p- ZrO_2 /p- Y_2O_3).^{13-15, 18} Combining two different host materials with different dopants can provide additional information about temperature-dependent phase changes, thereby helping to determine the thermal history.

In this work, we report on CO_2 laser-based T-Jump-induced phase changes in p-Eu: ZrO_2 /p-Tb: Y_2O_3 core/shell nanoparticles and their potential use as ex-situ thermosensors.¹⁵ In addition to temperature, we also evaluate the influence of heating time. Eu dopants are used with p- ZrO_2 because of the clear difference between the Eu^{3+}

$^5D_0 \rightarrow ^7F_J$ spectra in the tetragonal (t) and in the monoclinic (m) ZrO_2 phases. The appearance of these two phases is strongly dependent upon the material's thermal history.^{12, 16, 19} The metastable t- ZrO_2 phase is favorable at lower temperatures and shorter heating times, whereas the m- ZrO_2 phase is favorable at higher temperatures and longer heating times. Tb dopants are used with p- Y_2O_3 because Tb: Y_2O_3 has been shown to result in strong fluorescence.²⁰

2. Experimental and method

We synthesize precursor Eu: ZrO_2 /Tb: Y_2O_3 (p-Eu: ZrO_2 /p-Tb: Y_2O_3) core/shell nanoparticles using forced hydrolysis for the core, and homogeneous precipitation in the presence of the p-Eu: ZrO_2 core for the shell.^{10, 11} Since each shell is relatively thin, we repeat its synthesis three times. We use a NOVA nanoSEM 230 (FEI) scanning electron microscope (SEM) and a Tecnai G2 20 Twin TEM (FEI) transmission electron microscope (TEM) to evaluate the morphologies of the core/shell nanoparticles. The SEM is equipped with an X-Max Silicon Drift Detector (SDD) with an 80 mm² active area (Oxford Instruments, PLC.) for energy dispersive spectroscopy (EDS) measurements. We measure the x-ray diffraction (XRD) patterns of the samples using a PANalytical X'Pert Pro diffractometer (PANalytical B.V.) using Cu-K α radiation ($\lambda=1.5418$ Å) and operated at 45 kV/40 mA in combination with a PIXcel3D detector (PANalytical B.V.). The x-ray beam is collimated using a fixed divergence slit (FDS) with 0.04 radian Soller slits, 0.5° divergence slit, and a 10 mm mask, and is monochromatized using an X'Celerator monochromator (PANalytical B.V.).

We heat the nanopowder samples indirectly by enclosing them in pyrolytic graphite sheets (P13688-ND, 0.0028" thick, Panasonic Corp.). These sheets have a wide range of

operating temperature, high thermal conductivity (in-plane conductivity is 1000 W/mK), and high spectral absorption. These graphite sheets are held in place by thermally insulating (0.1 W/mK – 0.3 W/mK) alumina slabs (T-cast AA-30, 1/8" thick, Refractory Specialties, Inc.). The ceramic slabs have circular openings to provide direct access of the laser light to the sample holder and to minimize heat loss via conduction. To minimize oxidation of the sample holders during heating, we place them in a vacuum chamber at pressures between 5 Torr and 10 Torr. The sample holders are then heated using a 100 W CO₂ laser with wavelengths between 10.2 μ m and 10.7 μ m (Firestar series f100, Synrad, Inc.). The temperature of the nanopowder is monitored using a type K thermocouple, CHAL-005 (Omega Engineering, Inc.), which is also enclosed in the graphite sheet. The thermocouples are coated with a thin layer of very high temperature VHT primer (a division of Dupli Color, Inc., a Sherwin-Williams Company) to prevent short circuits. We use a HA400 temperature controller (RKC Instrument, Inc.) via the UC-2000 universal laser controller in closed-loop mode to regulate the laser power and the heating time.

Figure 1 shows images, schematics, and heating profiles of the laser based T-Jump heating technique. The powder sample is encapsulated inside a folded pyrolytic graphite sheet (Figure 1a). The continuous piece of pyrolytic graphite sheet quickly distributes the heat uniformly across its surface. A thermocouple wire is placed inside the folded graphite sheet. The graphite sheet itself is sandwiched between thermally insulating alumina slabs with circular windows to minimize contacts that could lead to additional heat loss, as well as for laser entry (Figure 1b). The PID loop configuration is shown in Figure 1c, and representative heating profiles are shown in Figure 1d.

Figure 1. (a) Sample configuration for laser heating of nanopowders and graphite sheet used to encapsulate the nanopowder with a thermocouple wire. (b) Assembled and disassembled part of the thermally insulating ceramic slabs. (c) PID loop configuration schematic. (d) Representative temperature profiles of isothermal heating using a closed-loop configuration.

Pyroprobe heating is performed using a CDS Analytical Pyroprobe 1000 using a ramp rate of 20,000 °C/s. The sample material (~5 mg) is placed inside a quartz tube, together with an Omega CHAL-005 thermocouple. The temperature is recorded via the thermocouple using an Omega RD8250 temperature recorder. Quartz wool is placed into the other end of the quartz tubes to prevent material from spilling out. The quartz tube is then placed inside the coil heater of the Pyroprobe 1000 and heated to the desired temperature, as described previously.¹⁶

For the laser based T-jump heating, the heat flow within the sample holder can be described according to a general form of energy conservation:²¹

$$\dot{E}_{in} + \dot{E}_g - \dot{E}_{out} = \dot{E}_{st} \quad (1)$$

where, $\dot{E}_{in}$ is the rate at which energy enters the control surface, $\dot{E}_g$ is the rate at which energy is generated by the control volume, $\dot{E}_{out}$ is the rate at which energy leaves the control surface, and $\dot{E}_{st}$ is the rate of change of energy stored within the control volume. $\dot{E}_g$ is assumed to be zero (i.e. heat generation is assumed negligible). Assuming that latent heat energy effects are not relevant, the rate of change of internal energy is given by $\dot{E}_{st} = \rho V c_p \frac{\partial T}{\partial t}$, where ρ is the density, c_p is specific heat at constant pressure, T is temperature, t is time, and V is the volume.

For a controlled heating experiment involving various temperatures and various heating times, we use temperature profiles that consist of: (1) a rapid rise in temperature (ramping), (2) a steady-state temperature (isothermal), and (3) a drop in temperature (cool down). Using equation 1 as a guide, the laser power needed to yield the desired three-stage heating profile should consist of: (1) Turn power on to $(\dot{E}_{in} + \dot{E}_{out})/\alpha$, (2) reduce power so that it is equal to $\dot{E}_{out}/\alpha$, and (3) turn off power, where α is the fraction of the energy absorbed by the sample holder. A proportional-integral-derivative (PID) controller is used to minimize the temperature deviation from the desired setpoint temperature. Figure 1d shows the temperature profiles obtained with the aid of the PID controller and which are used for the nanopowder heating experiments.

We measure the optical spectra as described elsewhere.¹⁶ Briefly, a Q-switched 10 ns pulse-length Nd:YAG laser (Continuum Corp.) operating at 10 Hz at 355 nm pumps a

Panther Optical Parametric Oscillator (Continuum Corp.). Using multiple mirrors, the Optical Parametric Oscillator output of the desired wavelength is directed onto the nanopowder sample which is contained in a glass vial. The fluorescence from the sample is collected using a 50 mm diameter lens with a focal length of 50 mm, collimated using a 50 mm diameter lens with a focal length of 500 mm, and focused onto the entrance slit of an Acton 2750 monochromator/spectrometer. The fluorescence spectra are acquired using a PMT (Hamamatsu R5108) and SpectraSense software (Princeton Instruments). The data is further processed using Origin Pro 9.1.

3. Results and discussions

3.1. As-synthesized samples

Figure 2a shows an SEM image of the p-Eu:ZrO₂/p-Tb:Y₂O₃ core/shell nanoparticles confirming the well-defined spherical morphology. Figure 2b shows the EDS spectrum, indicating that these particles consist mainly of Zr and Y – the Si peak is due to the substrate. The size distribution, as determined from the SEM images and shown in Figure 2c, indicates an average particle size of (240 ± 42) nm, consistent with our previous reports on rare-earth doped ZrO₂/Y₂O₃ core/shell nanoparticles.¹³

Figure 2. (a) SEM micrograph, (b) EDS spectrum, and (c) size distribution of the core-shell nanoparticles.

Figure 3 shows a TEM image and an XRD pattern of as-synthesized p-Eu:ZrO₂/p-Tb:Y₂O₃ nanoparticles. The particle surfaces of this material appear relatively smooth and the XRD pattern shows broad peaks indicating that the material is amorphous.

Figure 3. TEM image (a) and XRD pattern (b) of as-synthesized p-Eu:ZrO₂/p-Tb:Y₂O₃ nanoparticles.

Figures 4a and 4b show the fluorescence spectra of as-synthesized p-Eu:ZrO₂/p-Tb:Y₂O₃ core/shell nanoparticles excited at 488 nm and 533.6 nm, respectively. These excitation wavelengths preferentially excite 4f-4f transitions in Tb³⁺ and Eu³⁺ ions, respectively. The Tb³⁺ fluorescence is characterized by the ⁵D₄→⁷F_J (J=5-3) transitions with the ⁵D₄→⁷F₅ transition being the strongest intensity peak.²² The Eu³⁺ fluorescence is characterized by the ⁵D₀→⁷F_J (J=0-2) transitions with the ⁵D₀→⁷F₂ transition being the strongest intensity peak.²² All the fluorescence features are relatively broad and featureless, reflecting the broad inhomogeneous distribution of dopant sites in the amorphous host.

Figure 4. Fluorescence spectra of as-synthesized p-Eu:ZrO₂/p-Tb:Y₂O₃ core/shell nanoparticles excited at 488 nm (a) and 533.6 nm (b).

In order to characterize time- and temperature-dependent phase changes, we heat the as-synthesized p-Eu:ZrO₂/p-Tb:Y₂O₃ core/shell nanoparticles to various temperatures (200 °C, 400 °C, 600 °C, 800 °C, and 950 °C) for various heating times (2 s, 5 s, 10 s, 20 s, 30 s, 45 s, and 60 s) – see Figure 1d for the typical temperature profiles of these heating conditions. The initial temperature overshoot is less than 25 °C. The temperature deviation during the isothermal heating is within ± 5 °C. With a heating rate of 200 °C/s the temperature set point is reached within a few seconds.

3.2. Laser-heated samples

First, we characterize the p-Eu:ZrO₂/p-Tb:Y₂O₃ nanoparticles heated to the maximum temperature of 950 °C and the maximum heating duration of 60 s. Figure 5 shows the TEM image and the XRD pattern of this sample. As opposed to the as-synthesized nanoparticles, the surfaces of the heated material exhibit a grainy morphology and the XRD pattern shows narrow diffraction peaks indicating that the material is crystalline. The particles shown in the TEM image consist of agglomerations of smaller crystallites.

Figure 5. TEM image (a) and XRD pattern (b) of heated p-Eu:ZrO₂/p-Tb:Y₂O₃ nanoparticles. The black histograms correspond to the c-Y₂O₃ phase, and the red histograms correspond to the t-ZrO₂ phase.

The XRD peaks can be assigned to a combination of the tetragonal ZrO₂, t-ZrO₂, (PDF 01-079-1771) and cubic Y₂O₃, c-Y₂O₃, (PDF 01-083-0927) phases. The absence of the commonly observed monoclinic ZrO₂ (m-ZrO₂) phase can be attributed to the stabilization of the metastable t-ZrO₂ phase due to the Y₂O₃ shell, due to the small size, and due to doping with trivalent ions.^{12, 13} Above a critical size of about 10 nm to 30 nm, the tetragonal ZrO₂ phase can be stabilized via doping with trivalent impurities.¹⁹ The trivalent cation dopant generates oxygen ion vacancies that change the Zr⁴⁺ coordination number in the ZrO₂ structure from 7 (m-ZrO₂) to 8 (t-ZrO₂).

Figure 6 shows the fluorescence spectra of the heated p-Eu:ZrO₂/p-Tb:Y₂O₃ nanoparticles, excited at 488 nm and 533.6 nm, respectively. Compared to the as-synthesized material (see Figure 4), the increased degree of crystallization decreases the inhomogeneous broadening, and crystal-field induced energy level splits and shifts are now observed.⁹

Figure 6. Fluorescence spectra of heated (950 °C for 60 s) p-Eu:ZrO₂/p-Tb:Y₂O₃ core/shell nanoparticles excited at 488 nm (a) and 533.6 nm (b).

To aid in the assignment of the origins of the Eu³⁺ spectral features and phases, samples containing Eu³⁺ ions in pure t-ZrO₂, pure m-ZrO₂, and pure c-Y₂O₃ phases are prepared and their fluorescence spectra compared with those of p-Eu:ZrO₂/p-Tb:Y₂O₃ core/shell nanoparticles heated to 950 °C for 60 s, see Figure 7. The 606 nm and the 611 nm peaks are due to Eu³⁺ in the t-ZrO₂ phase and the c-Y₂O₃ phase, respectively. None of the peaks in spectrum 1 coincides with those of spectrum 3, indicating that the core/shell nanoparticles heated to 950 °C for 60 s contain no m-ZrO₂ phase.

Figure 7. (a) Fluorescence spectra obtained with 533.6 nm excitation of p-Eu:ZrO₂/p-Tb:Y₂O₃ heated to 950 °C for 60 s (1); Eu:t-ZrO₂ (2); Eu:m-ZrO₂ (3); and Eu:c-Y₂O₃ (4). (b) Corresponding x-ray diffraction spectra.

The fact that emission from Eu^{3+} in $\text{c-Y}_2\text{O}_3$ is observed in the $\text{Eu:ZrO}_2/\text{Tb:Y}_2\text{O}_3$ core/shell nanoparticles indicates diffusion of Eu ions from the core into the shell, bringing the Eu ions into close proximity to the Tb ions. This diffusion is further confirmed by the observation of energy transfer from Tb to Eu. We observe emission from Eu^{3+} for excitation of Tb^{3+} at 488 nm (see Figure 6a) even though Eu^{3+} does not absorb at this wavelength. Furthermore, we observe a reduction in the Tb^{3+} fluorescence lifetime in the heated core/shell samples. A $\text{Tb:Y}_2\text{O}_3$ reference sample heated to 950 °C for 60 s and excited at 488 nm shows a fluorescence lifetime, monitored at 542 nm, of 1.81 ms. A $\text{Eu:ZrO}_2/\text{Tb:Y}_2\text{O}_3$ core/shell sample heated and excited under the same conditions shows a fluorescence lifetime of 1.24 ms. Fluorescence lifetimes τ can be described by:

$$\tau = (k_r + k_{nr})^{-1} \quad (2)$$

where k_r is the radiative rate and k_{nr} is the non-radiative rate. Energy transfer from Tb to Eu adds to the k_{nr} contribution of Tb, thereby decreasing the observed lifetime.

Next, we compare the XRD patterns and fluorescence spectra of all the heated samples. Figures 8a and 8b show the XRD patterns of these samples and a temperature versus time phase diagram based upon these XRD patterns, respectively. Regardless of the heating times, all XRD patterns of samples heated to the same temperature overlap, indicating that they have the same phase. However, three distinct regions can be identified for samples heated to temperatures between 200 °C and 950 °C for 2 s to 60 s. Figure 8b shows these three regions: 1. amorphous ZrO_2 (a- ZrO_2) and amorphous Y_2O_3 (a- Y_2O_3); 2. tetragonal ZrO_2 (t- ZrO_2) and a- Y_2O_3 ; and 3. t- ZrO_2 and cubic Y_2O_3 (c- Y_2O_3), and Table 1 summarizes the conditions for these phases.

Figure 8. (a) XRD patterns and (b) temperature versus time phase diagram of the heated p-Eu:ZrO₂/p-Tb:Y₂O₃ core/shell nanoparticles. The histograms in (a) correspond to c-Y₂O₃ (black) and t-ZrO₂ (red) phases. In (b), three phase combinations of the core/shell nanoparticles are observed, 1. a-ZrO₂/a-Y₂O₃, 2. t-ZrO₂/a-Y₂O₃, and 3. t-ZrO₂/c-Y₂O₃. The spectrum numbers in (a) correspond to symbols in (b)

Table 1. Structural phases as determined by XRD patterns.

Temperature / °C	Heating time / s	Phases
200	10 – 60	a-ZrO ₂ , a-Y ₂ O ₃
400	10 – 60	
600	2 – 60	t-ZrO ₂ , a-Y ₂ O ₃
800	2 – 60	t-ZrO ₂ , c-Y ₂ O ₃
950	2 – 60	

Figure 9 shows the fluorescence spectra for the heated p-Eu:ZrO₂/p-Tb:Y₂O₃ core/shell nanoparticles when excited at 488 nm and 533.6 nm, respectively. Due to energy transfer from Tb to Eu, excitation at 488 nm results in the simultaneous fluorescence from Tb³⁺ ⁵D₄ → ⁷F_J (J=5-3) and Eu³⁺ ⁵D₀ → ⁷F_J (J=0-2) transitions. However, excitation with 533.6 nm results in fluorescence only from Eu³⁺ ⁵D₀ → ⁷F_J (J=0-2) transitions. The fluorescence-spectra-based phase assignments show more pronounced differences than the XRD-based phase assignments shown in Figure 8b.

Figure 9. Fluorescence spectra obtained with (a) 488 nm excitation and (c) 533.6 nm excitation. The different color symbols on the phase diagram show distinguishable regions corresponding to the fluorescence spectra obtained with (b) 488 nm excitation and (d) 533.6 nm excitation. The spectrum numbers on (a) correspond to symbols on (b). The spectrum numbers on (c) correspond to symbols on (d).

Excitation with 488 nm results in four distinct regions, see Figures 9a and 9b. Compared to samples heated to 200 °C (Region 1), samples heated to 400 °C (Region 2), show an additional shoulder at 547 nm. For the samples in region 3, the $^5D_4 \rightarrow ^7F_5$ transition shows the formation of two defined peaks at 543 nm and 550 nm. Moreover, the 613 nm peak blue shifts to 606 nm which indicates the formation of the t-ZrO₂ phase.¹² Based upon the shoulder at around 538 nm, one could potentially divide region 3 further into two distinct regions. However, it is worth noting that samples heated for short periods of time (2 s - 5 s), contain a large amount of ash, giving them a gray-white

rather than white appearance. The presence of the ash causes some of the baseline shift and could potentially also be responsible for the shoulder peak. As such, we leave all these samples in the same region. Samples in region 4 of Figure 9a and 9b show an additional fluorescence peak at 611 nm, coinciding with the formation of the c-Y₂O₃ phase (see Figure 5). ZrO₂ and Y₂O₃ crystallize below 600 °C and between 600 °C and 800 °C, respectively, see Table 1. The observation of crystalline Tb³⁺ emission for samples heated to about 600 °C and the appearance of the 611 nm peak due to Eu³⁺ emission following heating to 800 °C and above suggest inter-diffusion between p-Eu:ZrO₂ and p-Tb:Y₂O₃.

Excitation with 533.6 nm results in six distinct regions in the temperature versus time phase diagram, see Figures 9c and 9d. Regions 1 and 2 differ only by the presence of a small broad shoulder at 626 nm. The blue-shift of the Eu³⁺ emission peak from 613 nm to 606 nm during the transition from region 2 to region 3, represents the phase transition from a-ZrO₂ to t-ZrO₂, Figure 7a.¹² The spectra for regions 4 through 6 are very similar. The peak at 611 nm is due to Eu³⁺ in the c-Y₂O₃ phase. The main differences amongst the spectra for the three regions are the relative intensities of the 606 nm and the 611 nm peaks. For region 4, the 606 nm peak is much stronger than the 611 nm peak. The 611 nm peak appears as a shoulder peak. For region 5, the 606 nm peak is less or about the same intensity as the 611 nm peak. For region 6, the 606 nm peak is weaker than the 611 nm peak. The peak at about 617 nm in the region 4 spectra and one of the region 5 spectra is attributed to the glass sample holder used in the measurement. This peak is prominent in the samples that show low signal to noise ratio, particularly those that have been heated only for 2 s and 5 s and contain significant amount of ash due to incomplete calcination.

To determine whether it might be possible to improve the optical data by removing the ash from some of the samples, we conducted SEM and FTIR measurements on these samples. The SEM images show no apparent difference compared with the as-synthesized samples. The FTIR data shows an expected signal intensity decrease of volatile products (i.e., NO_2 , NH_3 , CO_2 and H_2O) for the heated sample, indicating that the metal salts have at least partially been transformed into metal oxides.^{13, 14} Thus, it is likely that the graying of the nanoparticles correspond to nanoparticles containing a mixture of metal oxides and metallic salt, making separation unlikely.

3.3. Pyroprobe-heated samples

Figure 10a shows the temperature profiles of p-Eu:ZrO₂/p-Tb:Y₂O₃ samples heated to three different temperatures via a pyroprobe heater. They are labeled **1**, **2**, and **3** for the subsequent discussion. Comparison of Figure 1d with Figure 10a shows that pyroprobe-heating takes longer to reach the set point temperature compared to laser-based T-jump heating. While the total pyroprobe heating time is set to 25 s, Figure 10a shows that it takes 15 s to 20 s to reach the maximum equilibrium temperature. The maximum temperatures for the three samples are **1**: 613 °C, **2**: 821 °C, and **3**: 949 °C and are held for only 5 s to 10 s.

The XRD of sample **1**, Figure 10b, shows that only t-ZrO₂ is present. This information is corroborated by the observation of the 543 nm and 550 nm peaks in the 488 nm excited fluorescence spectrum, Figure 10c, as well as the sole appearance of the 606 nm peak (no 611 nm peak) in the 532 nm excited fluorescence spectrum, Figure 10d. Accordingly, this sample can be placed in region 3 (600 °C/2 s - 60 s) and (800

$^{\circ}\text{C}/2\text{ s} - 5\text{ s}$) of Figure 9b, and more specifically placed in region 3 ($600\text{ }^{\circ}\text{C}/2\text{-}60\text{s}$) of Figure 9d.

Figure 10. (a) Temperature profile, (b) XRD pattern, and fluorescence spectra of pyroprobe heated samples excited (c) at 488 nm and (d) at 533.6 nm. **1**, **2**, and **3** refer to the three samples that are heated to various setpoint temperatures, according to the temperature profiles shown in (a).

The appearance of a shoulder peak at $2\text{ Theta}=29.1^{\circ}$ in Figure 10b for **2** and **3** indicates that the samples have been subjected to temperatures above $600\text{ }^{\circ}\text{C}$, Table 1. The presence of the $t\text{-ZrO}_2$ and $c\text{-Y}_2\text{O}_3$ phases are corroborated by comparison with the fluorescence spectra in Figures 9a and 9c. The 488 nm excited fluorescence spectra can be placed in region 4 ($800\text{ }^{\circ}\text{C}/10\text{ s} - 60\text{ s}$ and $950\text{ }^{\circ}\text{C}/2\text{ s} - 60\text{ s}$), while the 533.6 nm excited fluorescence spectra can be placed more specifically in region 5 ($800\text{ }^{\circ}\text{C}/10\text{ s} - 60\text{ s}$ and $950\text{ }^{\circ}\text{C}/2\text{ s} - 5\text{ s}$). Assuming that **2** and **3** have been heated for the same amount

of time, the relative peak intensities of the 606 nm and 611 nm peaks for the 533.6 nm excited spectrum suggest that **3** was subjected to higher temperatures.

4. Conclusions

Precursor p-Eu:ZrO₂/p-Tb:Y₂O₃ core-shell nanoparticles are prepared and subjected to rapid heating using a CO₂ laser-based T-Jump technique. The fluorescence spectra for two excitation wavelengths are used to prepare temperature/time phase diagrams, correlating irreversible phase changes in ZrO₂ and Y₂O₃ with heating temperature and duration. Compared to distinct phases that are identified in the XRD spectra, the fluorescence spectra revealed additional differences corresponding to differences in the dopants' energy levels that accompany the phase changes. This observation yields more diverse regions within the temperature/time diagram. Test samples show that the phase diagrams can be used to extract rough heating temperatures. However, in most cases no significant effect of heating duration for the investigated periods of 2 s to 60 s is observed. Refinements are expected from equipment upgrades for shorter heating durations, the use of spectral matching algorithms, and the application of kinetic analysis.

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