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Optical temperature sensing of Er^{3+}/Yb^{3+} doped $LaGdO_3$ based on fluorescence intensity ratio and lifetime thermometry

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ABSTRACT

The investigation of the fluorescence intensity ratio and the lifetime thermometry techniques for two rare earth perovskites-type oxide ($LaGdO_3:Er^{3+}$ and $LaGdO_3:Er^{3+}/Yb^{3+}$) has been carried out. We have demonstrated that the intensity ratio of thermally coupled levels of erbium ($^2H_{11/2}$ and $^4S_{3/2}$) is temperature dependant in the range from 283 to 393 K. The sensitivity parameter was found to reach a maximum value of 31×10^{-4} K^{-1} and 34×10^{-4} K^{-1} at 393 K and the temperature resolution to be equivalent to 1.61 and 3.1 K, for Er^{3+} and Er^{3+}/Yb^{3+} doped oxide, respectively. By studying the temperature dependence of the normalized lifetimes in the range from 293 to 348 K, we proved that the sensitivity of the green emission ($^4S_{3/2}$) is higher than the red one ($^4F_{9/2}$) for both samples, and that it increases from 144×10^{-4} K^{-1} for $LaGdO_3:Er^{3+}$ to 179×10^{-4} K^{-1} for $LaGdO_3:Er^{3+}/Yb^{3+}$. The thermal coefficients were quite large in comparison to those calculated for different luminescent materials and reported in literature. The repeatability of measurements was tested by performing heating and cooling cycles for both methods and the results show that these optical techniques have a good repeatability performance. Hence, the $LaGdO_3$: Er^{3+}, Yb^{3+} oxide has a precise and a satisfying sensitivity associated to a good thermal and chemical stability, suggesting that it can be a potential candidate in temperature sensing.

1. Introduction

The temperature sensing is of crucial importance in many areas of our daily life like medicine, biology, microelectronics, physics, and chemistry. Several of these fields require an accurate and high resolution measurement of temperature. However, the temperature evaluation represents sometimes an ambiguous task especially for hazardous, extremely hot or physically inaccessible objects. Therefore, the optical techniques, which are based on the control of optical properties variation of luminescent materials induced by temperature fluctuation, have been suggested in order to remedy these problems. The development of new luminescent probes with a very high accuracy and spatial resolution and based on a non-contact approach of temperature are consequently new challenges that we are facing today [1–3].

The non-contact luminescent thermometry can involve various spectroscopic techniques like IR thermography, thermoreflectance, optical interferometry, luminescence and Raman spectroscopy. These methods differ in their optical signals involved in temperature sensing and can include either the measurement of spectral features of luminescence (band position, shape and width, fluorescence intensity ratio, etc) or the temporal variation of luminescence (decay and rise time, etc) [1]. In particular, the temperature dependence of the fluorescence intensity ratio (FIR) technique has attracted the most attention of researchers. This interest is linked to the substantial sensitivity of luminescence on temperature and the simplicity with which the luminescence can be detected in comparison to other luminescence features. The FIR is based on the variation of emission intensity ratio, of thermally coupled levels with temperature. This process was frequently adopted due to its simplicity, good sensitivity and accuracy, since it eliminates problems related to excitation power and transmission fluctuation. In addition, the FIR technique allows a wide wavelength range spectra registration upon excitation with a relatively low cost continuous-wave laser [4].

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Otherwise, the fluorescence lifetime thermometry (Lt-th) is another efficient optical approach to measure temperature, which has many potential advantages. In fact, Lt-th avoids shortcomings related to non-homogenous materials since the fluorescence lifetime is independent on the phosphor concentration and is not affected by light scattering, reflection or by the intensity fluctuation [3,5]. However, Lt-th requires the implementation of pulsed excitation source that increase the setup cost.

The optical probes of temperature involve various fluorescent materials that can be organic like dye polymers [6–9] or inorganic such as phosphates [10], glass [11,12], fluorides [13] or oxides [14–16]. These optically active probes should fulfill the conditions of being with high thermal sensitivity and low fluorescence quenching. Rare earth doped oxides are promising materials, which have a good thermal and chemical stability and a low phonon energy, inducing a strong luminescence that depends fairly on the host matrix and its structure [17]. The lanthanides ions like Ho^{3+}, Tm^{3+} and Er^{3+} are the most commonly used for optical thermometry [18], since they emit in a large wavelength range from ultraviolet (UV) to near infrared (IR). They present interesting optical properties such as narrowband emissions and long luminescence lifetimes and were responsible for the well known up-conversion (UC) process. This phenomenon is based on the emission of high level energy in the ultraviolet–visible (UV-VIS) range under low energy excitation in the infrared. Erbium is an appropriate element frequently used for thermometry due to its green emission intensities of thermally coupled levels $^2H_{11/2}$ and $^4S_{3/2}$ [4] and to which the relatively low luminescence intensity is enhanced by co-doping with ytterbium.

In this work, we investigate the effect of Er^{3+} doping and Er^{3+}/Yb^{3+} co-doping $LaGdO_3$ rare earth oxide on optical sensing of temperature, by employing two methods based on fluorescence lifetimes or spectral properties. The Er^{3+} and Yb^{3+} co-doped materials, with perovskite like structure, have been examined as optical probes in some previous works reported in literature [2,19–22]. Particularly, the $LaGdO_3$ perovskite type oxide structure was studied for its structural, vibrational, electronic and electric properties [23–25], but it has not been considered for thermometry application. The choice of $LaGdO_3$ material is justified by the low phonon energy of matrix [23]. It is also explained by the fact that La^{3+} ion is optically inactive and that the Gd^{3+} ions emit in the UV range, which can avert possible interferences with the studied emission domain of Er^{3+}.

2. Experimental

The $LaGdO_3$ oxide doped with Er^{3+} (5%) and co-doped with Er^{3+} (5%) and Yb^{3+} (5%) have been synthesized using combustion method. The metal nitrates, employed as oxidizer, have been obtained by dissolving starting oxides weighed in stoichiometric ratio (Yb_2O_3 (Aldrich, 99.9%), La_2O_3 (PROLABO, 99.9%), Er_2O_3 (Ventron, 99.9%) and Gd_2O_3 (Aldrich, 99.9%)) in concentrated nitric acid. The glycine, used as a fuel, was added to the mixture after dilution with distilled water. The solution was maintained under magnetic stirring at 150 °C, to evaporate extra water. The formed gel was poured in a crucible and introduced into a furnace preheated at 600 °C. The powder resulting from combustion reaction was treated at 1000 °C during 6 h and characterized with X-rays diffraction (XRD) method on a PANAnalytical diffractometer operating with Cu Kα radiation (Cu; Kα = 1.5405 Å).

The optical properties of the prepared oxides were investigated by registering emission spectra under diode laser excitation at 980 nm. The emitted light was collected with a microscope objective (50×) and analyzed with a highly sensitive CCD camera (Synapse, Horiba) attached to a monochromator (iH320, Horiba). The luminescent lifetime measurements were carried out upon pulsed laser excitation at 980 nm. The emitted light was analyzed by monochromator after appropriate filtering. The decay curves were detected by a Hamamatsu R928 photomultiplier and measured with a digital oscilloscope. The thermal sensitivity was tested by using heating microscope stage within a temperature range from 283 K to 393 K and an accuracy of ±1 K.

2.1. X-ray diffraction analysis

Fig. 1 shows XRD patterns of Er^{3+}/Yb^{3+} doped and co-doped $LaGdO_3$ oxide. As it can be seen, major XRD peaks were indexed according to a monoclinic phase of $NdSmO_3$ structure which coincides with the standard data (JCPDS N°: 032- 0681). We note the presence of a second phase, where the peak positions correspond to the orthorhombic structure of $Nd_2Mo_2O_7$ (JCPDS N°: 035-0253). As a result, we can attribute the first phase to the $LaGdO_3$ perovskite type oxide [25] and the second one can be most likely assigned to the $La_2Gd_2O_7$ pyrochlore oxide [26].

3. Results and discussions

3.1. Optical properties

3.1.1. Upconversion (UC) emission study

The room temperature UC emission spectra of $LaGdO_3$: Er^{3+} and $LaGdO_3$: Er^{3+}/Yb^{3+} oxides were registered under diode laser excitation at 980 nm and a pumping power of 180 mW (Fig. 2a). As it can be seen, the samples exhibit intense green and red emission bands of Er^{3+} ions, which are attributed respectively to $^2H_{11/2} \rightarrow {}^4I_{15/2}$ (~530 nm), $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (~550 nm) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (~660 nm) transitions, with a significant increase in emission intensity for co-doped sample. The UC mechanism was fully described elsewhere and it is sufficient to note that the reason behind co-doping Er^{3+} with Yb^{3+} is to increase the emission intensity of erbium through energy transfer from Yb^{3+} to Er^{3+}. The population of the excited levels takes place after two photons excitation mechanism. In fact, under IR excitation at 980 nm, the energy ground state absorption (GSA) of erbium ($^4I_{15/2} \rightarrow {}^4I_{11/2}$) and ytterbium ($^2F_{7/2} \rightarrow {}^2F_{5/2}$) is occurred. From the $^4I_{11/2}$ level, an excited state absorption (ESA) of a photon induces the population

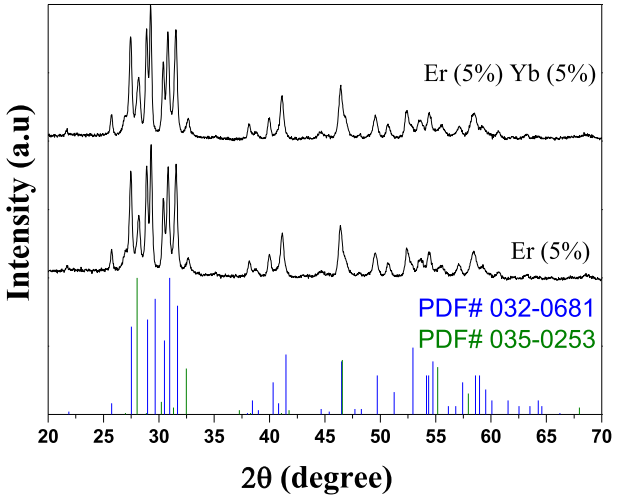

Fig. 1. X-ray diffraction patterns of the $LaGdO_3$:Er^{3+} (a) and $LaGdO_3$:Er^{3+}, Yb^{3+} (b) oxides treated at 1000 °C during 6 h. Reference files (PDF # 032-0681) and (PDF # 035-0253) are assigned respectively to monoclinic $NdSmO_3$ and orthorhombic $Nd_2Mo_2O_7$ oxides.