http://dx.doi.org/10.5935/0103-5053.20150190

J. Braz. Chem. Soc., Vol. 26, No. 12, 2405-2417, 2015.
Printed in Brazil - ©2015 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Review

Optically Detected Thermal Effects in Rare-Earth Doped Materials for Host Characterization, Thermometric Devices, Nanothermometry and Biothermometry

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We present a review of recent works on optically investigated thermal effects in crystalline and amorphous materials doped with trivalent rare-earth (RE) ions. The paper describes how the frequency upconversion (UC) photoluminescence (PL) technique is used to investigate the thermal behavior of samples and how to perform optical measurements of temperature. The UC technique is based on the sequential multiphoton absorption phenomenon that leads to anti-Stokes type emission. By measuring the relative intensity between UC emissions from thermally coupled RE energy levels, the absolute temperature of a sample can be determined. Research in this area is motivated by the possible uses of UC for basic characterization of materials and for noncontact thermometry using nanoscale devices as well as for biological and medical studies. Examples based on the application of bulk materials and nanopowders doped with several RE ions are presented.

Keywords: thermal population distribution, effective phonon mode, frequency upconversion, nano-and biothermometry

1. Introduction

1.1 Motivation

Thermal effects manifest themselves in condensed matter systems in a variety of ways, from the simple deposition of energy in a material due to light absorption, leading to local heating and temperature increase, to the opposite effect, where phonon-assisted light absorption leads to material's cooling. The first kind of process can be exploited for detecting nanoparticles with sub 10 nm sizes in diffraction limited optical systems,[1] while the second is used for laser cooling of solids.[2] There are in between a myriad of thermal processes and different ways to exploit and apply them.

Rare-earth (RE) ions in solid state matrices are often used for obtaining frequency down- and upconversion (UC)[3] of incident radiation,[4] obtaining laser at new wavelengths,[5] integrated optical systems and amplifiers[6] and to operate sensors for many physical quantities.[7] Indeed, RE ions are special optical probes because their 4f optically active electrons are shielded by more external electronic subshells, making them not very sensitive to their environment, but enough for observing changes which can be exploited for sensing applications. In this work, we focus on how thermal effects in RE doped materials are used for getting information about the materials in which they are embedded, for making thermometers in micro and nanoscopic scales and for getting thermal information in biological samples.

1.2 Statistical distribution of thermal population

The use of the spontaneous Raman scattering technique gives us interesting hints how to make spectroscopic studies in order to perform thermometry. In this scattering phenomenon, the incident laser photon with frequency ω_L is inelastically scattered by (but not exclusively) a molecule that can be excited to a high energy vibrational level associated to the electronic ground state manifold. In a simple picture, we consider two such vibrational levels: the ground state $|g\rangle$ and the first vibrational state $|e\rangle$ having energy larger than the ground state by the vibrational mode energy, $\hbar\Omega$. The laser photon may induce a transition through a virtual level $|v\rangle$, simultaneously generating a Stokes-shifted photon with frequency $\omega_L - \Omega$. As a result, the molecule ends in the vibrational excited state $|e\rangle$ and a quantum of molecular vibration (a phonon, in the sense of a quantum of molecular vibration) was created; therefore the molecular system becomes hotter. In another possible process the laser photon may interact with the molecule when it is in the vibrational excited state $|e\rangle$ driving it to the ground state $|g\rangle$ with the instantaneous emission of

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an anti-Stokes photon having frequency $\omega_L + \Omega$. The final result is that the vibrational excitation (the phonon) has been annihilated and the molecule gets colder.

The occupation probability distribution of the molecules' energy levels as a function of the temperature T, described by the Maxwell-Boltzmann statistics, is given by

$$N_{|e\rangle}(T) = N_{|g\rangle} e^{-\hbar\Omega/kT} \quad (1)$$

In this case, one speaks in terms of "thermally coupled energy levels" associated with the states |g> and |e>, meaning that a non-negligible fraction of the total population in the ensemble of molecules can reach the |e> level due to available thermal energy in the system. Then, in spontaneous Raman scattering, since the intensity of the Stokes and anti-Stokes emissions are proportional to the population of molecules in the states |g> and |e>, respectively, if one knows the molecule vibrational modes' energies activated in the Raman process and records the intensities of the Stokes and anti-Stokes Raman signals, one gets immediately the temperature of the molecular ensemble. For example, CS_2 presents a very strong Raman mode at 658 cm^{-1} related to the molecular stretching mode. Considering equation 1, at 300 K a fraction of 11.2% of the molecules is thermally kept in the |e> vibrational level, so that the Stokes/anti-Stokes intensity ratio is approximately 8.

The above features are also observed in the case of solid-state matrices, in which one defines phonons in the sense of solid state physics - a quasi-particle with energy and momentum, representing the collective oscillations of the crystalline matrix. Nonradiative (NR) transitions of an atom/ion in a matrix from lower energy levels to higher energy levels and the contrary have their energy gaps bridged by the absorption (annihilation) or emission (creation) of matrix phonons, cooling or heating the matrix, respectively. This means that if a pair of energy levels of an element embedded in a matrix is thermally coupled and in any given previous characterization experiment (absorption spectrum, for example) one measures the energy difference between these two levels, by recording the photoluminescence (PL) intensity originated from these states or Raman spectrum one can determine the sample's temperature. Conversely, if one knows the sample's temperature, one can get information about the matrix phonons, their density of states, etc.

2. Rare-Earth Doped Materials for Basic Host Characterization

We now turn our attention to thermal studies of RE doped materials, aiming at solid-state spectroscopy: matrix characterization and thermometry. For these purposes, we start by reviewing how the solid-state matrix should be considered in order to take into account multiphononic transitions.

2.1 The phonon density of states, maximum energy phonon mode *vs.* effective phonon mode

The study of multiphonon (MP) assisted processes in RE doped materials has been the subject of much interest. In the past, PL and frequency UC mediated by phonons have been analyzed by Auzel *et al.*[8-11] They demonstrated that it is possible to induce PL in solids doped with RE ions even when the difference between the excitation frequency and the electronic transition frequency is larger than the maximum phonon frequency of the host material. This was observed both for transitions involving creation or annihilation of phonons. For understanding and modelling such MP transitions, one should take into account the temperature dependence of the involved parameters. Indeed, the nonresonant absorption cross-section is given by[12]

$$\sigma(T) = \sigma^0[exp(-\hbar\omega/kT) - 1]^{-q} \quad (2)$$

where σ^0 is the resonant absorption cross-section, $\hbar\omega$ is the energy of the cutoff phonons (discussed below), k is the Boltzmann constant and q is the number of phonons needed to bridge the nonresonant gap in the absorption process. Further, the MP excitation rates should be written as[13]

$$R_{ij}(T) = [exp(\hbar\omega/kT) - 1]^{-q_{ij}} \quad (3)$$

where q_{ij} is the number of phonons involved in the MP excitation from level i to level j. Finally, the population relaxation rates $\gamma(T) = \gamma^{rad} + W^{nrad}(T)$ must take into account the temperature dependence of the NR decay rates $W^{nrad}(T)$ as[8]

$$W^{nrad}(T) = W^{nrad}(T_0)\left[\frac{1-exp(\hbar\omega/kT)}{1-exp(\hbar\omega/kT_0)}\right]^{-q}, \quad (4)$$

where q is the number of phonons involved in the NR relaxation to the lowest lying energy level and $W^{nrad}(T_0)$ is the NR decay rate determined by using the energy gap law,[14,15] known at a given temperature T_0.

The idea that the cutoff mode would dominate the phonon-assisted processes is based on the fact that these processes are described in the framework of perturbation theory, and that, e.g., processes involving two phonons would be a second-order perturbation process, then being less probable than one phonon process (which would be a

first-order perturbation process). Thus, the phonon-assisted process involving phonons with highest energy (the cutoff phonons) would be more probable than, for example, a relaxation process involving two phonons with half of the energy of the cutoff phonon.

However, with this argumentation one forgets to consider the phonon density of states, that is, the number of phonon modes *per* unit frequency *per* unit volume of real space. It can happen that the number of cutoff phonons is so small compared with the number of phonons with, say, half of this energy that, effectively, all phonon modes are responsible for promoting the NR transitions. Then, contrarily to what was generally thought it was shown[8-11] that MP assisted processes should be described in terms of an "effective phonon mode" (EPM), or "promoting mode", with a frequency smaller than the cutoff phonon frequency of the host material. This EPM would represent a kind of weighted average between the phonons energies and their respective populations, being a characteristic of each and every matrix. This has been verified in many studies.[16-18] Moreover, studies of phonon-assisted UC in RE doped nanocrystals (NCs) revealed that, for a given temperature, the UC spectrum changes as a function of the NCs' size, indicating that the phonon density of states changes due to quantum confinement effects,[19] thus changing the EPM energy and corroborating the assumption that the EPM dominates the MP process in condensed matter systems.

2.2 Thermal characterization of glasses, crystals and ceramics

The vast majority of studies on phonon-assisted optical processes in RE doped matrices that we are interested in was made by exploiting the two green emissions of trivalent erbium ions, Er^{3+}, at ca. 525 and ca. 545 nm that correspond to transitions from the excited states $^2H_{11/2}$ and $^4S_{3/2}$ to the ground state $^4I_{15/2}$, respectively. The states $^2H_{11/2}$ and $^4S_{3/2}$ are thermally coupled and typically separated by ca. 750 cm^{-1} that does not vary much in different hosts due to the nature of RE ions. This means that, at room temperature, by resonantly exciting the ions to the $^4S_{3/2}$ state, ca. 8.2% of its population will be thermally promoted to the $^2H_{11/2}$ state. The ratio between the PL intensities at ca. 545 and ca. 525 nm can thus be written as[20]

$$R = \frac{I_{525\,nm}}{I_{545\,nm}} = C\exp\left(-\Delta E/kT\right), \tag{5}$$

where ΔE is the energy gap between the levels $^2H_{11/2}$ and $^4S_{3/2}$ and C depends on the levels' lifetimes and electronic weights. The experimental technique is sometimes referred to as fluorescence intensity ratio (FIR). It offers some practical advantages over alternative techniques available for performing thermometry like fluorescence lifetime measurements, since, among other reasons, for all cases of interest, it is immune to excitation light intensity fluctuations and it can be used with continuous wave (CW) excitation. Besides this, its detection scheme requires basically only two photodetectors, eventually with spectral filters which select the wavelength to be registered by each detector. On the other hand, for performing lifetime measurements, for example, besides the need to use a pulsed (or at least modulated) excitation source a stage in the apparatus able to register the photodetector signal as a function of the time is required. As will be discussed in a later section, the performance/sensitivity of thermal sensors based on the ratio between PL intensities starting from thermally coupled levels depends on this factor C and the energy gap ΔE. One relationship very often used for quantifying the performance of optical thermometers based on the PL intensity ratio, R, is the so-called sensor sensitivity (or relative sensitivity) S_R, commonly defined in the literature as

$$S_R = \frac{dR}{dT} = R\frac{\Delta E}{kT^2}, \tag{6}$$

and another quantitative performance index is the sensitivity (or absolute sensitivity), which is defined as

$$S = \frac{1}{R}\frac{dR}{dT} = \frac{\Delta E}{kT^2}. \tag{7}$$

One strategy to improve the performance of the optical thermal probes is the use of codoped samples. In this case, ytterbium ions, Yb^{3+}, are mostly used since they present a reduced number of excited states, resulting in large transition oscillator strength.[21] This makes Yb^{3+} good absorbers of radiation at ca. 980 nm. The energy levels of Yb^{3+} are close enough to Er^{3+} levels such that the energy transfer (ET) rates from Yb^{3+} to Er^{3+} are larger than the radiative absorption rates of the Er^{3+} if they were the lone dopants of the matrix. Nevertheless, for the sake of matrix characterization, singly doped systems are also investigated.

2.2.1 Singly doped systems

2.2.1.1 Er^{3+} doped systems

Matrices in the glassy, nanocrystalline and ceramic phases have been extensively studied. Tripathi *et al.*[22] investigated ET among Er^{3+} under excitation of a Ti:sapphire laser emitting at 800 nm (resonant with the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ transition) in a bismuth oxide based glass and how it leads to the population of the canonical Er^{3+} thermally coupled levels (CETCL). Besides this, the authors exploit the thermal coupling of the two Stark sublevels of $^4S_{3/2}$, which

are ca. 263 cm^{-1} far apart and compare the thermometric performance with that using the CETCL. Similar study was made for a tellurite glass.[23] In another work[24] the behaviors of UC emissions in the ultraviolet and in the visible were examined as a function of the temperature in a tellurite glass and the role of a temperature dependent NR relaxation rate described by equation 4 is evidenced. The behavior of the emissions from CETCL was recorded but no comparison of the results with the literature was made.

By resonantly exciting Er^{3+}:ZnO NCs at 978 nm,[25] the authors investigated the effect of different annealing times on the samples' optical properties using the emissions from the CETCL. They concluded that longer annealing times influenced the ZnO nanocrystalline structure thus changing the energy gap between the CETCL. Thermometric studies were made leading to a thermometer sensitivity of 0.62% K^{-1}. Ceramics, which are composite materials consisting of a glassy host with crystalline micro- and nano-inclusions, have also been investigated. The thermometric studies reported by Zou *et al.*[26] present a comparison of the intensities ratio between the PL from levels $^2H_{11/2}$ (emission at 532 nm) and each of the two Stark sublevels of $^4S_{3/2}$ (emissions at 544 and 554 nm). It was verified that the maximum sensitivities were 0.37 and 0.17% K^{-1}, respectively, and the reasons for that were discussed in terms of substitutional sites of the ceramics.

2.2.1.2 Systems doped with other rare-earth ions

The use of RE ions other than Er^{3+} is less common. Holmium ions, Ho^{3+}, present a pair of thermally coupled levels $^5F_4$ and $^4S_2$ with an energy gap of ca. 240 cm^{-1} that emit light respectively at ca. 538 and ca. 545 nm due to transitions to the ground state $^5I_8$. The ratios of PL intensities emitted from these levels in Ho^{3+} doped tellurite glass were compared[27] with thermocouple measurements in the range 265-383 K and a good agreement in the temperature measurement was found. In order to extend the temperature range in which the tellurite glass still can be used as the thermal probe, the authors included PbO_2 and $BaCO_3$ as glass modifiers, and observed that the temperature range could be extended up to 450 K, but the accuracy of the temperature measurements decreased.

There are also reports on the use of europium ions, Eu^{3+}, as the single dopant for thermal characterization of a solid state matrix. $NaEuF_4$ phosphor has been investigated[28] and the transitions from the thermally coupled levels $^5D_1$ and $^5D_0$ to the ground state manifold ^7F_J (J = 0-4) - emissions in the range 500-560 and 570-690 nm, respectively, were analyzed as a function of the sample's temperature for all lines. Using equation 2 and applying the same fit parameters for all samples, the energy gap between levels $^5D_1$ and $^5D_0$ could be measured as $(1.69 \pm 0.11) \times 10^3$ cm^{-1}, agreeing well with the theoretical value of 1734 cm^{-1}.

Neodymium ions, Nd^{3+}, were also used as thermal probes in condensed matter systems. Kumar *et al.*[29] excited the Nd^{3+} hosted in a lithium-tellurite glass at 800 nm (resonant absorption $^4I_{9/2} \rightarrow {}^4F_{5/2}$) and observed among other PL lines the phonon-assisted upconverted emission at 766 nm (transition $^4G_{7/2} \rightarrow {}^4I_{15/2}$). No measurements of relative intensities were performed, but solely the intensity of the emission at 766 nm. By varying the sample's temperature from 298 to 523 K a 90-fold enhancement in the emission at 766 nm was observed. Characterization of the thermometer sensitivity was made as well as time resolved measurements as a function of temperature. In another work[18] the same kind of experiments was performed, but dealing with a tellurite glass and reporting a 670-fold enhancement in the emission at 754 nm when changing the samples' temperature from 200 to 535 K. Aiming at a comparison with other reports, a parameter called luminescence enhancement to temperature interval (LETI) was defined, leading to a LETI = 2.00 K^{-1}, the largest ever reported in such systems. A rate equation model was proposed to explain the mechanism behind this particular UC emission and excited state absorption cross-sections were estimated. The EPM of the tellurite matrix was determined as ca. 700 cm^{-1}, smaller than the cutoff phonon energy of ca. 850 cm^{-1}.

2.2.2 Codoped systems

2.2.2.1 Yb^{3+}/Er^{3+} codoped systems

In the codoped systems, the resonant excitation of Yb^{3+} is usually performed at ca. 980 nm. The energy absorbed by the Yb^{3+} is transferred to Er^{3+} and the UC processes are triggered. This codoping strategy is frequently used in glassy hosts. dos Santos *et al.*[30] used a chalcogenide glass to perform thermal studies using a less common excitation scheme at 1064 nm. This wavelength is still within the absorption band of Yb^{3+} but is red-detuned relative to the absorption peak at ca. 980 nm. The PL intensities ratio from the CETCL was monitored as a function the samples' temperature. A high sensitivity of 0.52% K^{-1} at 443 K was obtained thanks mainly to the excitation scheme, which makes the system even more dependent on the absorption of phonons in order to bridge the energy gaps of the transitions involved in the UC process exploited for thermometry. The PL from the CETCL as a function of the temperature of the oxyfluoride glass matrix was studied[31] and their potentialities for thermometric applications were evaluated. Also the intensities ratio between both green emissions and that in the red at 659 nm, corresponding to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}, were evaluated. A fluorophosphate glassy

host was the choice where a detailed spectroscopic study[32] including the Judd-Ofelt analysis, infrared spectroscopy, PL at different excitation schemes and lifetime measurements were presented; the green and red emissions of Er^{3+} as a function of temperature were studied in detail.

Yb^{3+}/Er^{3+} codoping was also used to study the crystalline phase, like where the authors used a codoped crystalline sapphire fiber in order to determine the PL intensity ratio between the red and green emissions of Er^{3+} to measure temperatures up to 1,420 K.[33] In another study[34] a La_2O_3 phosphor was characterized and the thermal behavior of the CETCL was investigated, stressing that this material can be used for thermometric applications up to 600 K. In a very interesting work,[35] the authors studied individual $NaYF_4$ codoped microspheres, with diameters between 0.7 to 2.0 μm, using an inverted microscope with the capability of heating the samples. Again, the green emissions of Er^{3+} were monitored as a function of temperature. Surface effects, more drastic for smaller microspheres, were also analyzed. Glass ceramics were also studied. An oxyfluoride matrix containing Yb^{3+}/Er^{3+}:$NaYF_4$ NCs was reported[36] and among other characterization studies thermal experiments with the green emission lines of Er^{3+} were performed. The potential of the transparent glass-ceramics was evaluated for photonic and thermometric applications. Sodium-niobium-tellurite glass-ceramics were characterized in details by differential thermal analysis, X-ray diffractometry, Raman spectroscopy, scanning electron microscopy, optical absorption and lifetime measurements.[37] The thermal behavior of both green emissions besides the red emission of Er^{3+} was studied when exciting the samples at 980 nm for characterization of the UC mechanisms responsible for generating these emissions.

2.2.2.2 Yb^{3+}/Ho^{3+} codoped systems

Although not as frequently as Er^{3+}, holmium ions, Ho^{3+}, were used as codopant with Yb^{3+} for UC studies in a variety of matrices. An amorphous codoped calcium aluminate phosphor synthesized using solution combustion process was studied.[38] Strong multicolored (blue, green and red) UC emission due to Ho^{3+} ions is observed, showing tunability (from green to red) depending on the excitation power. The color tunability is a consequence of an induced local heating due to laser absorption; the temperature changes were measured using the FIR method. The temperature could be sensed through two pairs of thermally coupled levels in Ho^{3+}, producing green PL ($^5F_4$, $^5S_2 \rightarrow {}^5I_8$) around 550 nm and the other in the blue ($^5G_4$, $^5G_5 \rightarrow {}^5I_8$) around 475 nm. β-$NaLuF_4$ crystalline microprisms were investigated by Zhou *et al.*[39] Studies on the temperature dependence of two thermally coupled multiplets ($^5F_1$, $^5G_6$ and $^5F_{2,3}$, $^3K_8$) were carried out from 390 to 780 K. The large energy difference (1,438 cm^{-1}) between the thermally coupled levels could account for a higher relative sensitivity in this system than most RE doped materials. The authors in another study[40] made the characterization of an oxyfluoride matrix containing β-PbF_2 NCs; in this matrix the NR decay rates are smaller than in other materials, enhancing the efficiency of UC processes, including those exploited in the applications based on the thermally coupled levels of Ho^{3+} from 303 to 643 K.

2.2.2.3 Other Yb^{3+} codoped systems

In optical spectroscopy, thulium ions, Tm^{3+}, are often considered when one is interested in the blue region of the spectrum. In the case of thermometry with Yb^{3+}/Tm^{3+} the excitation scheme is more complex than in the previous cases. The thermal sensitivity of the emissions from Tm^{3+} is due to the fact that the ET mechanism from the sensitizer Yb^{3+} to the Tm^{3+} is nonresonant and demands participation of phonons. Such mechanism was reported for a codoped tellurite glass.[41] The FIR between the PL at 478 nm (transition $^1G_4 \rightarrow {}^3H_6$) and at 651 nm (transition $^1G_4 \rightarrow {}^3F_4$) was measured *vs.* the temperature and helped clarify the mechanisms related to the diverse UC emissions. In another set of experiments using $LiNbO_3$ single crystals as host,[42] another pair of thermally coupled levels in Tm^{3+} was exploited from 323 to 773 K. In this case, PL at ca. 700 nm ($^3F_{2,3} \rightarrow {}^3H_6$) and ca. 800 nm ($^3H_4 \rightarrow {}^3H_6$) were found to be thermally coupled. A theoretical model was used for obtaining the gap between the thermally coupled levels, leading to 2,160 cm^{-1} which is compared to the value 1,805 cm^{-1} obtained from the UC spectra.

Nd^{3+} can also be used as thermal probes in condensed matter systems. In the same way as codoping with Tm^{3+}, codoping with Nd^{3+} enables the exploitation of phonon-assisted ET from Yb^{3+} to Nd^{3+} which produces a temperature dependent UC spectrum. The group of Nd^{3+} thermally coupled levels ($^4F_{7/2}$, $^4S_{3/2}$; $^4F_{5/2}$, $^2H_{9/2}$; and $^4F_{3/2}$) decay to the ground state $^4I_{9/2}$ emitting PL at ca. 754, 805 and 866 nm, respectively.[15,17] Xu *et al.*[40] studied these thermally coupled levels and how they are influenced by temperature changes in oxyfluoride glass-ceramics containing β-PbF_2 NCs and characterized the UC emissions spectrally and temporally. It was verified that the presence of the NCs enhances the UC emission as compared to the precursor glass. In another work[43] an unusual and interesting approach was used. Instead of using Yb^{3+} as sensitizers, this role was played by the Nd^{3+} and the emission of Yb^{3+} was monitored in experiments with yttrium silicate crystalline powders.

Even less common is the use of terbium ions, Tb^{3+}, to characterize host materials due to the complexity of Tb^{3+} energy level structure and, in the case of codoping

with Yb^{3+}, the large energy mismatches between both ions. Nevertheless, cooperative ET followed by UC in a fluoroindate glass host was studied[17] where a large temperature dependence of the Tb^{3+} emissions at ca. 417 nm (transition $^5D_3$, $^5G_6 \rightarrow {}^7F_5$) and ca. 454 nm (transition $^5D_4 \rightarrow {}^7F_5$) was observed when exciting the samples with radiation at 1064 nm, red-detuned from resonance, but still in the absorption band of the Yb^{3+} ions. A rate equation model taking into account temperature-dependent cross-sections and relaxation rates was proposed. The experimental data showing the behavior of the Tb^{3+} emissions from 308 to 530 K were explained with a single fitting parameter, the EPM energy of the glass. It was verified that the data could not be adjusted to the theoretical model when the cutoff phonon energy was used, corroborating the relevance of the EPM concept. More recently, by exciting a germanate glass at 976 nm, multicolor PL due to Tb^{3+} was studied and the role played by different UC mechanisms was investigated from 278 to 523 K.[44] The authors observed the emergence of competing phenomena like the increase of the Yb^{3+} absorption cross-section as the temperature increases accompanied by deleterious effects for UC due to energy migration among the sensitizers and MP excitation of Tb^{3+} in the ^7F_J (J = 0-4) manifold.

Interesting behavior was observed in triply-doped systems like the one reported by Xing *et al.*[45] In this work, $NaNbO_3$ single crystals were simultaneously doped with Yb^{3+}, Ho^{3+} and Tm^{3+} aiming at the observation of multicolor PL. By exciting the samples at 980 nm and changing the samples temperature from 289 to 773 K white light emission was obtained.

To close this section, we mention that there are also reports on thermal studies in other codoped systems, like Yb^{3+}/Pr^{3+},[46] and Yb^{3+}/Sm^{3+},[47] but they will not be discussed due to the space limitation in this paper.

3. Rare-Earth Doped Materials for Thermometric Applications

This section is devoted to explicit uses of RE doped systems for thermometric applications. We start with proof-of-principle experiments, followed by applications in nanothermometry and biothermometry.

3.1 Thermometric devices

3.1.1 Singly doped systems

3.1.1.1 Er^{3+} doped systems

The majority of reports related to the use of RE doped materials for thermometry uses the method of FIR, where the PL emitted from thermally coupled levels (or manifolds) is detected and their ratio is calculated, thus giving a measure of the material's temperature as indicated in equation 5. This leads to, e.g., immunity against the excitation laser intensity fluctuations. The optical thermometers operated in this way are suitable for uses in electromagnetically noisy environments like inside high power voltage transformers or for noncontact temperature measurements inside systems having micrometer dimensions.

Many reports use glasses as matrices for RE ions that probe the temperature. For instance, Maciel *et al.*[20] use an Er^{3+} doped fluoroindate glass with different doping levels for temperature measurements from 296 to 448 K by exciting the samples at 1,480 nm, resonant with the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+} ions. The CETCL were reached after ET among three and four Er^{3+} and the FIR between the green emissions at ca. 522 nm (transition $^2H_{11/2} \rightarrow {}^4I_{15/2}$) and ca. 543 nm (transition $^4S_{3/2} \rightarrow {}^4I_{15/2}$) was recorded as a function of the samples' temperature. The sensitivity measured was 0.52% K^{-1}, which is high for singly doped materials. Another glassy system was investigated[48] where the same transitions were exploited, but the samples were excited at 800 nm. Temporal measurements were also made since the dynamics of the UC process may influence the thermometer performance. Sensitivities of the same order of magnitude as those determined by León-Luis *et al.*[48] were obtained applying the same excitation and detection schemes, but using a very common silicate glass as host; a thermometer operating from 296 and 633 K presenting a maximum sensitivity of 0.23% K^{-1} was obtained.[49] An integrated optoelectronic approach was used in order to operate a thermometer based on a silica-on-silicon waveguide.[50] The same excitation and detection schemes used in the two previously cited papers were used and the maximum sensitivity of the device was 0.9% K^{-1} at 430 K, larger than the reported sensitivities for a thermometer based on bulk silica. The authors of another study[51] operated a sensor based on a chalcogenide glass excited by commercial low cost, low power semiconductor lasers emitting at 1,540 nm, operating between 293 and 493 K and presenting an accuracy of 0.3 K, besides analyzing the role played by the host matrix in the sensor's performance.

An excitation laser at 980 nm was used to study the infrared-to-visible UC in lead lanthanum-zirconate-titanate transparent ceramics.[52] The emissions from the CETCL have wavelengths ca. 534 and ca. 565 nm, red shifted in relation to what normally is observed in glassy systems. The ceramic matrix allowed the thermometer to be operated at high temperatures around 885 K with moderate sensitivity of 0.4% K^{-1}. The ceramic system $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ was employed[53]

which used basically the same approach as de Camargo *et al.*[52] but reached the maximum temperature of 443 K and sensitivity of 0.44% K^{-1}. However, electrical characterization of the material was made which is an important step for the future use of the system as optoelectronic device.

3.1.1.2 Systems doped with other rare-earth ions

As mentioned before, for materials investigated to be used in thermal sensing devices, it is much less common to use RE ions other than Er^{3+}. However, Ho^{3+} ions were used as dopant of a tellurite based glass.[54] The excitation was performed at 890 nm (resonant with the transition $^5I_8 \rightarrow {}^5I_5$ of Ho^{3+}) and the intensities of the emissions at ca. 538 nm (transition $^5F_4 \rightarrow {}^5I_8$) and at ca. 543 nm (transition $^5S_2 \rightarrow {}^5I_8$) were monitored as a function of the temperature, which varied in the range 265 K < T < 363 K. The addition of PbO_2 and $BaCO_3$ to the matrix, making it harder, extended this range up to ca. 450 K. Another approach was used where the authors applied a Tm^{3+}:YAG crystal integrated to optical fibers to build a temperature sensor.[55] The excitation light at 785 nm was intensity modulated by a mechanical chopper and was sent through the fiber to excite the crystal; the PL signals at ca. 1,880 and ca. 1,470 nm, corresponding to the Tm^{3+} ions transitions $^3F_4 \rightarrow {}^3H_6$ and $^3H_4 \rightarrow {}^3F_4$, respectively, were collected through the fiber for temporal analysis. With this scheme, the temporal resolution achieved was ca. 2 μs. The Tm^{3+} emissions were spectrally separated by filters and sent to different photodetectors to record the PL dynamics. It was observed that due to the increase of the sample's temperature, the PL decay times were reduced from several ms to 0.2 ms when the temperature varied from room temperature to 1,473 K, with an average sensitivity of 3 μs K^{-1}.

3.1.2 Codoped systems

3.1.2.1 Yb^{3+}/Er^{3+} codoped systems

This codoping strategy is by far the most used when investigating materials aiming at devices. Unless otherwise specified, the strategy is to resonantly excite the Yb^{3+} at ca. 980 nm and to observe UC from the Er^{3+} due to the ET $Yb^{3+} \rightarrow Er^{3+}$; sometimes UC is also observed due to the simultaneous multiphoton excitation of the Er^{3+}. The CETCL are populated and the PL intensity ratio between the green emissions due to the transitions $^2H_{11/2} \rightarrow {}^4I_{15/2}$ (ca. 525 nm) and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (ca. 545 nm) is measured as a function of the samples' temperature.

Working with a codoped ZBLA glass multimode fiber as a sensor element butt-coupled to a multimode silica fiber, Berthou *et al.*[56] operated a thermometer up to 473 K and characterized the UC process that leads to the green emissions in details. The FIR was measured as a function of the temperature as usual. A chalcogenide glass from which optical fibers can be pulled was investigated[51] where a Nd^{3+}:YAG laser at 1064 nm was employed as excitation source for the thermometer operating from 293 and 493 K and presenting a maximum sensitivity of 0.52% K^{-1}. In another study,[57] besides colorimetric and color tunability studies of the UC emissions in a tungsten-tellurite glass under excitation at 808 nm, the authors performed measurements from 300 to 690 K exciting the glass at 980 nm. The sensitivity achieved was 0.29% K^{-1}. In an interesting work,[58] the authors used microspheres of codoped niobium-borate glass. Whispering-gallery modes (WGM) resonant with the CETCL emissions were analyzed under different temperatures from 290 to 380 K. The band shapes and the WGM resonances were temperature dependent and shifts of 4.7 pm K^{-1} were observed, induced by heating due to the excitation laser. The FIR method was also used for comparison reasons; a temperature resolution of 0.7 K was obtained in the FIR technique, while a 100 times better resolution was obtained for the WGM method.

In general, crystalline hosts allow temperature sensing up to higher temperatures than glasses. Many applications reported involved micro and nanocrystalline matrices, with measurements performed on ensembles of particles. Dong *et al.*[59] used alumina particles for performing thermometry at high temperatures, up to 973 K using the FIR technique. They measured a sensitivity of 0.51% K^{-1} and a resolution of 0.3 K when exciting the particles with a laser diode emitting at 978 nm. In the same way, TiO_2 codoped particles were used for performing FIR based thermometry.[60] By adding Li^+ to the host they observed a strong PL enhancement and used such matrix for measurements up to 925 K with a sensitivity of 0.25% K^{-1}. Following the same line, another group used the same approach to study a Yb^{3+}/Er^{3+}:Gd_2O_3 nanocrystalline phosphor, measuring sensitivities of 0.39% K^{-1} and temperatures up to 900 K.[61]

The β-$NaYF_4$ matrix is known to be an efficient upconverter when doped with Er^{3+} or codoped with Yb^{3+}/Er^{3+}. Recently β-$NaYF_4$ microsprisms were used to make thermometry using the FIR technique but in a less common temperature range, from 160 to 300 K.[62] The maximum sensitivity was 1.20% K^{-1}, higher than usually found due to the operation at low temperatures (see equation 6). The heating effects due to the laser absorption were investigated and it was observed that they were not significant for the thermometer operation. An yttrium-niobate phosphor codoped with Yb^{3+}/Er^{3+} was studied[63] where not only UC but also downconversion emissions were studied. In the material characterization, measurements using the FIR

scheme were performed from 300 to 573 K and a high sensitivity of 0.73% K^{-1} was obtained.

Also recently, looking for a new appropriate material to be used for optical thermometry,[64] the authors employed a Yb^{3+}/Er^{3+} codoped polycrystalline $CaWO_4$ for obtaining UC emissions at ca. 384 and ca. 408 nm, corresponding to $^4G_{11/2} \rightarrow {}^4I_{15/2}$ and $^2H_{9/2} \rightarrow {}^4I_{15/2}$ of Er^{3+}, respectively. The FIR technique was used to characterize the system from room temperature to 873 K, leading to a maximum sensitivity of 0.73% K^{-1}. The same group published another work with the same material following the canonical techniques for thermometry and demonstrated the use of the polycrystalline samples for temperature measurements from 294 to 923 K with a maximum sensitivity of 0.92% K^{-1}.[65]

Yb^{3+}/Er^{3+} doped zincate phosphor (Yb^{3+}/Er^{3+}: $Ba_5Gd_8Zn_4O_{21}$) was characterized, including the UC spectroscopy.[66] The CETCL emissions were recorded as a function of temperature and a maximum sensitivity of 0.24% K^{-1} was measured. This sensitivity is not high, but the color of the samples changed in a large spectral range from red to yellow/green when the temperature is tuned. Also interesting is the work[67] where the authors reported a detailed study of the UC processes observed and applied the Judd-Ofelt theory for determining the matrix optical parameters. Following the standard FIR technique, they determined a maximum sensitivity of 0.8% K^{-1}. SrF_2 was also studied in the temperature range from 295 to 695 K and a sensitivity of 0.396% K^{-1} was measured.[68] Finally, a La_2S_3 matrix was spectroscopically characterized and its properties as a thermometer investigated in the temperature range from 110 to 900 K, leading to a sensitivity of 0.75% K^{-1}.[69]

Also ceramic materials have appeal for applications in thermometry, since they may combine the best characteristics of glassy and crystalline materials. An optical temperature sensor based on the infrared-to-visible UC in Er^{3+}/Yb^{3+} co-doped Bi_3TiNbO_9 ceramics was reported.[70] The FIR method applied to the green emissions of Er^{3+} ions from 123 to 693 K resulted in a maximum efficiency of 0.32% K^{-1}. The same investigation strategy was used in another work,[71] where yttrium-silicate crystalline ceramic powders prepared by combustion synthesis was used as a thermometer operating in the range 300 to 600 K, leading to a maximum sensitivity of 0.56% K^{-1} under continuous-wave excitation and 0.70% K^{-1} under pulsed excitation; the different sensitivities were attributed to the heating due to larger irradiation. In another study[72] $Na_{0.5}Bi_{0.5}TiO_3$ ceramics were studied from 93 to 613 K and a sensitivity of 0.31% K^{-1} was achieved.

3.1.2.2 Yb^{3+}/Ho^{3+} and Yb^{3+}/Tm^{3+} codoped systems

In this section we describe a less common class of codoped thermometers. One example of interest was reported[73] using a Ho^{3+} doped $CaWO_4$. Since intense blue emissions from the ($^5G_6$, $^5F_1$) and ($^5F_{2,3}$, $^3K_8$) states to the $^5I_8$ ground state of Ho^{3+} are easily excited, the thermometric behavior based on the FIR was studied. The temperature dependences of the blue emissions were measured in the range 303-923 K, with a maximum sensitivity of 0.5% K^{-1}. A similar work was presented[74] where $Ba_{0.77}Ca_{0.23}TiO_3$ ferroelectric ceramics were used as thermometer matrix. An unusual temperature range from 93 to 300 K was explored, and a maximum sensitivity of 0.53% K^{-1} was verified.

Crystalline yttria doped with Tm^{3+} was investigated[75] under continuous-wave illumination at 976 nm. The FIR technique, applied to the blue UC emission lines at 476 and 488 nm, originated from the thermally coupled Stark sublevels $^1G_{4(a)} \rightarrow {}^3H_6$ and $^1G_{4(b)} \rightarrow {}^3H_6$, respectively, was exploited to operate a thermometer working in the range 303 to 753 K with a maximum sensitivity of 0.35% K^{-1}. The use of oxyfluoride glass-ceramics codoped with Yb^{3+} and Tm^{3+} was reported[76] where the Yb^{3+} ions were excited at 980 nm and UC emissions at 700 and 800 nm (respectively the $^3F_{2,3} \rightarrow {}^3H_6$ and $^3F_{2,3} \rightarrow {}^3H_4$ transitions on Tm^{3+} ions) were detected. The FIR was measured from 293 to 703 K and a large sensitivity of 3.3% K^{-1} was observed, that is, according to the authors, the largest for thermometers using that technology at that time.

3.1.2.3 Other Yb^{3+} codoped systems

A non-conventional codoping strategy, using two different species as acceptors, was reported[77] where the behavior of a $Yb^{3+}/Ho^{3+}/Tm^{3+}$ codoped matrix was investigated. Again, Yb^{3+} were used as sensitizers and the goal was the exploitation of thermally coupled levels belonging to Ho^{3+} and Tm^{3+}. The combination of three RE ions allows management of the effective energy level structure of the system. In this case, the triply-doped yttria matrix was submitted to temperatures from 303 to 703 K; a maximum sensitivity of 0.69% K^{-1} and a relative sensitivity of 0.34% K^{-1} were obtained. The same strategy was adopted[78] where microcrystalline $Yb^{3+}/Tm^{3+}/Gd^{3+}$ doped $NaLuF_4$ was applied to exploit the FIR in the ultraviolet region. As usual, Yb^{3+} were used as sensitizers to successively transfer energy to Tm^{3+} which were used as ladders to reach excited levels near 37,000 cm^{-1} ($^3P_{2,1,0}$). Then the highly excited Tm^{3+} transfer their energy to the ^6I_J (J = 15/2, 13/2, 11/2, 9/2 and 7/2) Gd^{3+} energy levels, which are thermally coupled. In the temperature range investigated (298 to 523 K) the sensor showed a sensitivity of only 0.04% K^{-1}. Other transitions in the blue were also used for thermal sensing but in all cases, the sensitivity was small.

3.3 Nanothermometry

This section is devoted to review papers focusing in thermometry in the nanoscale. A very good survey in this subject is found in Jaque and Vetrone,[79] which however does not limit itself to RE doped systems.

Er^{3+} still is the mostly used probe in singly-doped nano and micrometer sized systems. In the past, Alencar *et al.*[80] used $BaTiO_3$ NCs and observe the green emissions from the CETCL when exciting the ensembles at 980 nm, studying crystalline powders with grains of different average sizes. By varying the samples' temperatures from 322 to 466 K, using the FIR technique they observed that the sensitivity of such sensors depends on the size of the NCs. This was explained considering modifications of NR relaxation mechanisms with the NCs size. Five years later, working with Er^{3+}:$NaYF_4$ NCs having different sizes, Schietinger *et al.*[19] verified the effect of quantum confinement of phonons, corroborating the analysis made before.[80] In another study,[81] the authors observed that inserting molybdenum into the $Yb_2Ti_2O_7$ matrix one sees an enhancement of the green emission originated in the CETCL due to the fact that Mo ions contribute as an extra ET channel for excitation of the CETCL. The study was based on the FIR technique applied from 290 and 610 K with a sensitivity of 0.74% K^{-1}. An interesting work was reported,[82] where Er^{3+}:Y_2O_3 NCs were synthesized and their thermometric performances using the CETCL were compared before and after re-calcination of the powders. After re-calcination, the green UC lines were 56 times stronger, and the sensor sensitivity was doubled, reaching 0.4% K^{-1}. This procedure proved that OH^- groups on the NCs surface are greatly reduced by re-calcination, and the presence of these groups promotes depopulation of ions in upper energy levels by efficient ET processes from Er^{3+} to OH^-.

A large number of reports on Yb^{3+}/Er^{3+} codoped systems is available. For example, Yb^{3+}/Er^{3+}:ZrO_2 NCs were used to obtain a high sensitivity of 1.34% K^{-1} operating the thermometer from 323 to 673 K, exploiting the FIR technique between Stark levels associated with the green and red emissions from the Er^{3+}.[83] Yttria NCs doped with Yb^{3+}/Er^{3+} were synthesized and analyzed in details.[84] The NCs properties before and after a calcination process were measured. Using the FIR technique for the CETCL and varying the temperature from 315 to 555 K, the sensitivities were determined and a large improvement for calcined samples was verified. The maximum sensitivity were 1.8% K^{-1}. Yttria NCs were also used for thermometry in a wide temperature range (93 to 613 K).[85] Also recently one group claimed that $BaGd_2ZnO_5$ NC is the best matrix for thermometry based on ET-UC.[86] However, they used Yb^{3+}/Er^{3+} doped $BaGd_2ZnO_5$ as temperature sensor from 350 to 800 K and obtained a small sensitivity of 0.31% K^{-1}. Another trial for identification of a high sensitivity thermometer was reported[87] where using Yb^{3+}/Er^{3+} doped $GdVO_4$ nanoparticles a maximum sensitivity of 1.11% K^{-1} was obtained, smaller than the sensor based on calcined samples of Yb^{3+}/Er^{3+} doped yttria.[84]

Besides Er^{3+} and Yb^{3+}/Er^{3+} other doping strategies were tried for temperature sensing using NCs. Particular attention is deserved by Zhou *et al.*[88] where an original approach to achieve high sensitivities was presented. Since, by definition, the relative sensitivity of optical thermometers is proportional to the energy gap between the thermally coupled levels used in the FIR technique, the authors proposed a new strategy by using the UC emissions that are originated from two multiplets with energies having opposite temperature dependences.[88] Then, by using Tm^{3+} in β-$NaYF_4$:20% Yb^{3+} core-shell nanoparticles under excitation at 980 nm, a relative sensitivity of 1.53% K^{-1} from 350 to 510 K was obtained.

3.4 Biothermometry

The investigation of physical and/or chemical processes inside a cell is not a trivial task, and in the recent past years, many experimental techniques were developed to extract relevant information from cells. One important information is the temperature, which for example may indicate inflammatory processes inside the cell that may trigger cell diseases. So, measuring temperature inside cells is a challenge for modern biology. In this section, we highlight works which directly apply the thermometric techniques discussed so far in the present paper aiming at getting biological information.

A recent review paper stresses how UC with RE doped NCs can be used not only for highly sensitive bio- and chemical sensing, like detection of biomolecules (avidin, ATP), ions (cyanide, quicksilver), gases (oxygen, carbon dioxide, ammonia), but also for *in vitro* temperature sensing, by using the FIR technique with the Er^{3+} UC emissions in the green.[89] An interesting paper shows how Yb^{3+}/Er^{3+} codoped $NaYF_4$ NCs can be used inside HeLa cervical cancer cells for monitoring their temperature in a colloidal solution.[90] The FIR between the green emissions from Er^{3+} was used. A pump-and-probe scheme was used for inducing heating in the cells, which were killed when the colloidal temperature achieved 45 °C. The excitation at ca. 980 nm is also convenient for light penetration in the tissues purpose. Thermal images were also made, in which for each diffraction-limited spot a spectrum was taken and the FIR calculated. In this kind of application the influence of the cell environment is very important. Preliminary

studies in this direction were reported in another work, where the authors used Er^{3+}:$BaTiO_3$ NCs to study the role of the NCs' sizes and the surrounding medium on the green PL for different temperatures.[91] The studies were performed with the NCs in air and inside liquids of biological interest, like water and glycerol.

Yb^{3+}/Er^{3+} co-doped Gd_2O_3 NCs were used to increase the temperature in the environment and for its simultaneous measurement.[92] The temperature increased up to 504 K, due to absorption of excitation photons and the phonon-assisted relaxations, and was measured using the FIR technique monitoring the strong green PL due to the Er^{3+}. The authors claim that the controlled optical heating of NCs and its nanovolume has large potential for applications such as localized hyperthermia and in the creation of nanoscale holes in soft media. The proposal was confirmed by a work which studied the UC process and the FIR of nanoscopic Er^{3+}:$Y_3Ga_5O_{12}$ in the biological temperature range (292 to 335 K) and stressed that one needs to keep the RE doping level low in order to avoid heating of the medium by the thermometer.[93] Considering the possibility of induced heating Sedlmeier *et al.*[94] characterized Yb^{3+} sensitized Er^{3+}/Ho^{3+}/Tm^{3+}:$NaYF_4$ NCs and suggested their use for thermally activated intracellular drug delivery conjugated with thermal sensing. In the same line, the use of multifunctional $NaYF_4$:Yb^{3+},Er^{3+}@Ag core/shell nanoparticles was proposed.[95] In this hybrid material, by absorption of light, silver would induce a large local heating, while the RE part would sense the resulting temperature. Convincing results were shown where Yb^{3+}/Er^{3+} doped YVO_4 NCs were used simultaneously as high performance nanoheaters and nanothermometers, presenting a high sensitivity of 1.2% K^{-1} and a high induced heating (from 315 to 460 K) within a small excitation power interval from ca. 13 to 50 W cm^{-2}.[96] Based on the obtained results, the authors claim that Yb^{3+}/Er^{3+}:YVO_4 NCs are indicated for therapeutics.

A different approach for performing thermometry in biological systems was adopted by Benayas *et al.*[97] Water dispersible Nd^{3+}:YAG NCs were excited at 808 nm and the PL at 938 and 945 nm, due to Nd^{3+} transitions starting from Stark levels of the manifold $^4F_{3/2}$ to the ground state, were recorded as a function of the NCs temperature. Taking advantage of the large downconversion efficiency over that of the UC processes, it was demonstrated that this system allows an easy-to-use thermometer in the biological spectral window. Other functionalities were introduced by Haro-González *et al.*,[98] where the authors present a potential biosensor which could be optically manipulated. Silica nanospheres having diameter of ca. 590 nm, singly- or co-doped with Er^{3+}, Eu^{3+} or Tb^{3+}, were employed as a thermometer using the FIR technique on the respective transitions, but presenting the possibility of being positioned at will inside a biological structure by the use of optical tweezers. The thermometric properties of the analyzed particles were studied and good sensitivities up to 3% K^{-1} (in the case of Er^{3+} doped silica nanospheres) were achieved.

4. Summary and Conclusions

This short review paper summarizes some works on the characterization of thermal effects in rare-earth doped materials aiming possible applications of the materials as optical thermometers. Several examples of glasses and crystals - bulk samples and nanoparticles - were described. The results reviewed here were obtained exploiting the frequency upconversion phenomenon that is observed in media doped with trivalent rare-earth ions excited by lasers operating in the infrared region.

The temperature measurements in the cases considered were based on measurements of the intensity ratio between the photoluminescence emitted by pairs of thermally coupled levels of RE ions embedded in various hosts. Resonant and nonresonant excitation of the active RE ions, energy transfer and phonon-assisted (excitation and relaxation) electronic processes were considered in order to describe the results of the several experiments. Absolute temperatures were determined assuming that the population distribution of the RE emitting levels is in quasi-thermal equilibrium, determined by the Maxwell-Boltzmann statistics, due to the interaction between the RE ions and the host medium. The given examples illustrate applications of the fluorescence intensity ratio technique in solids and bio-molecules. From the collection of results summarized here the reader may identify possible lines for future work in order to achieve better optical thermometers. The existing challenges for obtaining temperature sensors with larger sensitivities were mentioned and we hope that the herein highlighted features may stimulate the synthesis and use of new materials that may present better characteristics for operation of more efficient devices in the future.

Acknowledgements

We acknowledge financial support from the Brazilian agencies Conselho Nacional de Desenvolvimento Cientifico e Tecnológico (CNPq) and Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco (FACEPE). The work was performed in the framework of the National Institute of Photonics (INCT de Fotônica) project and PRONEX/CNPq/FACEPE.

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Submitted: June 15, 2015
Published online: July 31, 2015