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Characterization of Er^{3+} and Nd^{3+} doped Strontium Barium Niobate glass ceramic as temperature sensors

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Temperature sensor is a vast group of the commercially approachable optical sensors. Recently has appeared a new kind of these devices using the fluorescence intensity ratio (FIR) with a very good sensitivity. The FIR technique has been carried out in Strontium Barium Niobate (SBN) glass ceramic sample to extend the knowledge of this kind of matrix. The samples has been doped with Erbium and Neodymium ions (2.5 mol%). The thermalized level $^4S_{3/2}$ ($^2H_{11/2}$) of Er^{3+} ions was studied in a wide temperature range from 300 K to 700 K with a maximum sensitivity of 0.0017 K^{-1} for 600 K. In these ions the FIR technique has been applied to the transitions $^2H_{11/2} \rightarrow {}^4I_{13/2}$ and $^4S_{3/2} \rightarrow {}^4I_{13/2}$ at 800 nm and 850 nm, respectively. The weak overlap between these thermalized emission bands is an important factor to reduce the error in the measurements. In the Nd^{3+} doped sample, the emission bands corresponding to the $^4F_{5/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions were analyzed as a function of the temperature from 300 K to 700 K with a maximum sensitivity of 0.0015 K^{-1} for 600 K. These results are compared with other optical devices using FIR technique.

1. Introduction

Trivalent Rare Earth (RE^{3+}) doped materials have received significant attention for optical temperature sensors due to their fluorescence intensity temperature dependence. In the past decades, a number of optical temperature sensors have been presented and the most outstanding approach is based on the fluorescence intensity ratio (FIR) technique [1–4], which can help to reduce the influence of measurement conditions and therefore, improve the measurement sensitivity. Several researcher groups have developed their investigation in the application of this technique on RE^{3+}-doped materials. Rai et al. [5] have presented an investigation of a possible application of yellow intensity ratio of Pr^{3+} doped tellurite glass to high dynamic range temperature sensing. Tripathi et al. [6] have presented a temperature sensor based on FIR technique of the upconversion emission of Sm^{3+} ions. Kusama et al. [7] discussed the FIR techniques for temperature monitoring using Y_2O_2S: Eu phosphor as the sensing medium within 100–300 K temperature range. The first work using the thermally coupled $^2H_{11/2}$ and $^4S_{3/2}$ levels of Er^{3+} was reported by Bethou and Jorgensen [1]. In this paper the authors used the FIR technique in fluoride hosts doped with these ions exciting either 488 nm or 970 nm over the 293–473 K temperature region. Also Aigouy et al. have reported applications of FIR technique as thermal micro-imaging devices with Er:Yb codoped nanocrystals and glasses [8,9].

The aim of this work is to extend the knowledge of Strontium Barium Niobate (SBN) glass ceramic as a temperature sensor. SBN ceramics have large pyroelectric and linear electro-optic coefficients, as well as strong photorefractive effects [10–12]. They are ferroelectric materials, with Curie temperatures ranging from 320 to 470 K for bulk samples, when $0.25 < x < 0.73$ [13]. Piezoelectric properties with large spontaneous polarization of this material are of great interest because there were no volatilization problems, which has been one of the major problems in lead-based perovskite materials [14]. Its lead-free composition also makes it environmentally friendly.

Two samples of this matrix, doped with Er^{3+} and Nd^{3+} ions, were studied in the temperature range from 300 to 700 K in order to explore a new possibility of optical temperature sensor based on the FIR technique. Usually the Er^{3+} ions have been analyzed as optical temperature sensor using the visible emissions coming from the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions. However, these emission bands show a large overlap between them and it is difficult to obtain the intensities of the areas as function of temperature. Therefore, in this work have been used the $^2H_{11/2} \rightarrow {}^4I_{13/2}$ and $^4S_{3/2} \rightarrow {}^4I_{13/2}$ transitions at around 800 nm and 850 nm, which ones are far from the excitation wavelength of a doubled Nd^{3+}: YAG laser. Moreover, as can be seen in the emission spectra, the overlap between these emission bands from Er^{3+} ions is nearly negligible. Therefore, it is expected to reduce the error in the intensity

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measurements. Respect to the Nd^{3+} ions, to our knowledge, few works have studied their possibilities as optical temperature sensor. In this work it is shown that these ions have many possibilities in order to be used in a SBN glass ceramic matrix as optical temperature sensor in the 300–700 K range and at even higher temperatures.

2. Experimental

The RE_2O_3–SrO–BaO–Nb_2O_5–B_2O_3 glasses were prepared using the melt-quenching method, where RE represents Er^{3+} or Nd^{3+} ions [15,16]. Commercial powders of reagent grade were mixed and melted in platinum crucible during 1 h inside an electric furnace at 1400 °C. The melt was poured between two flat iron plates with separation of 1.6 mm. The precursor glass samples were polished to obtain a smooth and flat optical grade surface. The glass ceramics were obtained by thermal treatment of the primary glass samples at 620 °C during 2 h in an electric furnace.

The SBN glass ceramic samples were excited with a commercial continuous wave 532 nm Diode Pumped Solid State laser (DPSS) at low power. The Er^{3+}: ${}^2H_{11/2} \rightarrow {}^4I_{13/2}$ (800 nm) and ${}^4S_{3/2} \rightarrow {}^4I_{13/2}$ (850 nm) and Nd^{3+}: ${}^4F_{5/2} \rightarrow {}^4I_{9/2}$ (820 nm) and ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ (880 nm) transitions were measured and recorded using a 0.32 m CCD spectrograph.

High temperature measurements were performed by placing the SBN glass ceramic samples inside an electric furnace to increase the temperature from room temperature (RT) to 700 K at a rate of 1 K/min.

3. Results and discussion

3.1. Theoretical background

The low cost of the material fabrication and the easy pumping condition by using low-cost Diode Pumped Solid State laser have increased the interest in the development of rare earth doped matrix for temperature sensors. In these materials many pairs of energy level with small separation of the order of the thermal energy are known. For practical sensors, the energy levels are not only optically coupled to the ground state but also have a relatively small separation with a high probability of non-radiative transition between the two levels of the pair.

The technique used in this work to calibrate the temperature sensor is the FIR. In this technique, the fluorescence intensities of two closely spaced energy levels are recorded as a function of the temperature to be analyzed in a simple three-level system (see Fig 1). The small energy gap between these two levels allows the upper level to be populated from the lower level by thermal excitation. The ratio of these intensities is independent of the source power intensity since these ones are proportional to the population of each level involved. The relative population between the two levels, R, follows a Boltzmann-type population distribution given by:

$$R = \frac{I_{31}}{I_{21}} = \frac{\omega_{31}^{R} g_3 h\nu_3}{\omega_{21}^{R} g_2 h\nu_2} \exp\left(\frac{-E_{32}}{KT}\right) = C \exp\left(\frac{-E_{32}}{KT}\right) \quad (1)$$

where K is the Boltzmann constant, E_{32} is the energy gap between these two excited levels (see Fig. 1), g_3 and g_2 are the degeneracies $(2J+1)$ of the levels, ω_{31}^{R} and ω_{21}^{R} are the spontaneous emission rates of the E_3 and E_2 levels to the E_1 level, respectively.

The rate at which the ratio changes with the temperature is:

$$S = \frac{dR}{dT} = R\left(-\frac{E_{32}}{KT^2}\right) \quad (2)$$

This expression represents the sensor sensitivity, S. From Eq. (2), it is clear that the sensitivity increases when there is a large energy difference E_{32}. However, as the energy difference become larger, the population and the intensity from the upper level decreases and other optical processes could appear.

3.2. Experimental results: Er^{3+} ions

The literature indicates that there are only a few rare earth ions which can be used for sensitive temperature measurements. The most common is the case of the erbium doped materials, which have been extensively studied as temperature sensor [1,8,9,17–19]. The Fig. 2 shows the emission spectra of the Er^{3+} doped SBN sample in the NIR range at RT and at 600 K. The two emission bands at 800 nm and 850 nm correspond to ${}^2H_{11/2} \rightarrow {}^4I_{13/2}$ and ${}^4S_{3/2} \rightarrow {}^4I_{13/2}$ transitions of Er^{3+} ions, respectively. Due to the small energy gap of 748 cm^{-1} between these two levels (obtained from absorption spectrum), the thermalization of ${}^4S_{3/2}$ (${}^2H_{11/2}$) levels occurs.

An analysis based on a simple three-level system comprised of the ${}^4I_{13/2}$ (level 1), ${}^4S_{3/2}$ (level 2) and ${}^2H_{11/2}$ (level 3) has been carried out. The ratio between the intensities of the fluorescence at 800 nm and 850 nm can be related to the temperature T as according to Eq. (1). This relation was checked by recording the emission spectra at different temperatures from 300 to 700 K for the SBN glass ceramic sample (see Fig 3). From the fit of these experimental data to Eq. (1), the values of $C = 4.07$ and $E_{32} = 872.3$ cm^{-1} have been found. This value for the energy gap is in good agreement with the value obtained from the absorption spectrum (748 cm^{-1}). The sensor sensitivity is defined by Eq. (2) and the curve of sensitivity versus T is shown in Fig. 4. At the

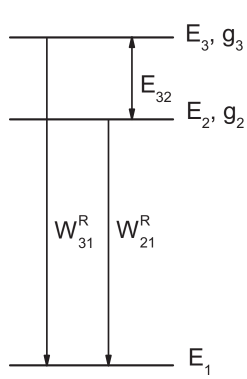

Fig. 1. Simplified diagram for three levels.

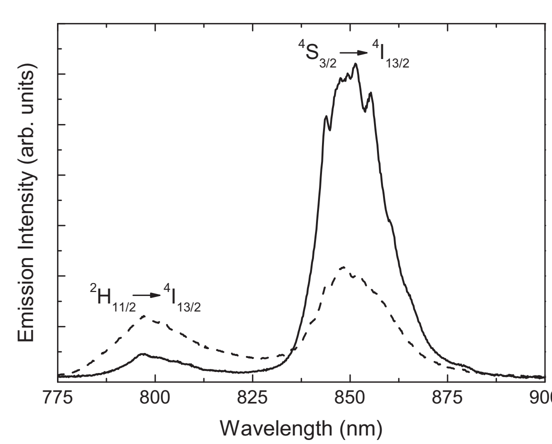

Fig. 2. Emission spectra in the NIR range for 2.5 mol% Er^{3+} at RT (straight line) and 600 K (dashed line) with excitation at 532 nm.

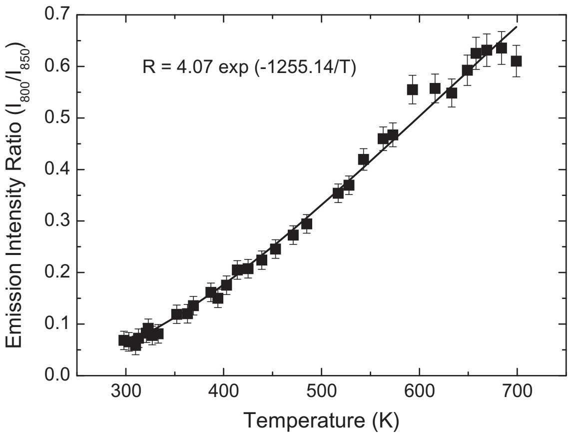

Fig. 3. Intensity ratio of the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions as a function of temperature (■). The solid line is the fit to Eq. (1).

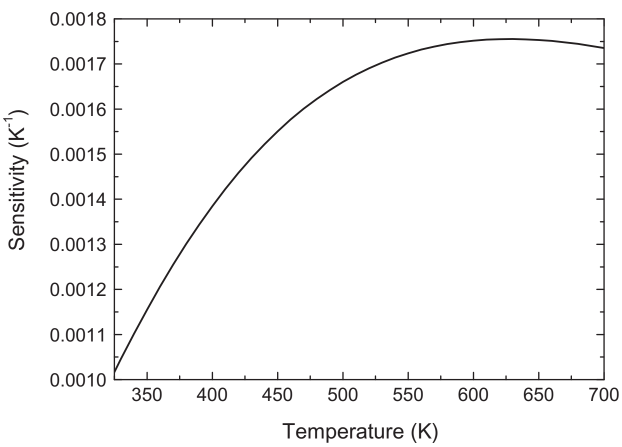

Fig. 4. The sensor sensitivity as a function of temperature of Er^{3+} doped SBN glass ceramic.

temperature of 600 K, the sensitivity of Er^{3+} doped SBN glass ceramic reached the maximum value about 0.0017 K^{-1}.

The researcher groups have tried to improve the fluorescence efficiencies of Er^{3+} doped sensor material using different host matrices [20–22]. Dong et al. have reported a maximum sensitivity of 0.0052 K^{-1} at 476 K of Er^{3+} doped Al_2O_3 in an upconversion process by exciting the sample at 978 nm [19]. In Er^{3+}–Yb^{3+} codoped silicate glasses, Li et al. have reported a maximum sensitivity of 0.0033 K^{-1} at 296 K [23] using upconversion processes. In these previous works have been used the emission bands in the visible region which ones overlap between them. In this work, as can be seen in Fig 2, the thermalized bands at low and high temperature are well differentiated and the error in the application of the FIR technique is minimized.

3.3. Experimental results: Nd^{3+} ions

The Nd^{3+} ion has two close levels, $^4F_{5/2}$ and $^4F_{3/2}$, with an energy separation lower than 1000 cm^{-1} [24,25]. In the studied sample, a value of 995 cm^{-1} from the absorption spectrum has been obtained for the energy gap between these two levels. This gap allows the population of the upper level from the lower due to thermal excitation. The Fig. 5 shows the emission spectra of Nd^{3+} doped SBN glass ceramic sample at RT and at 600 K. The two emission bands at 820 nm and 880 nm correspond to $^4F_{5/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions of Nd^{3+} ions, respectively. In the same way than

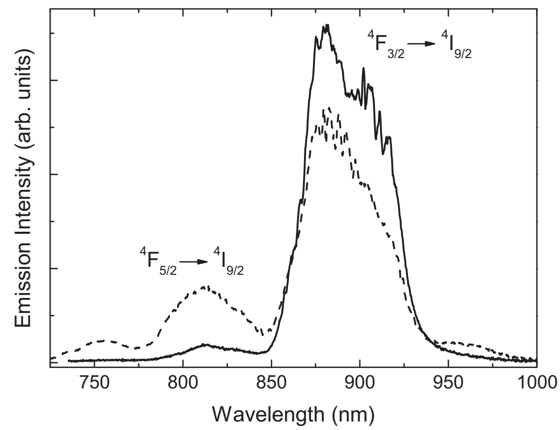

Fig. 5. Emission spectra in the NIR range for 2.5 mol% Nd^{3+} at RT (straight line) and 600 K (dashed line) with excitation at 532 nm.

the Er^{3+} ions, an analysis based on a simple three-level system compromised of the $^4F_{5/2}$ (level 3), $^4F_{3/2}$ (level 2) and $^4I_{9/2}$ (level 1) has been carried out. The ratio of these emission bands have been related to the temperature T according to Eq. (1) from 300 K to 700 K and are presented in Fig. 6. As can be seen, the weak overlap between these thermalized emissions bands allows the

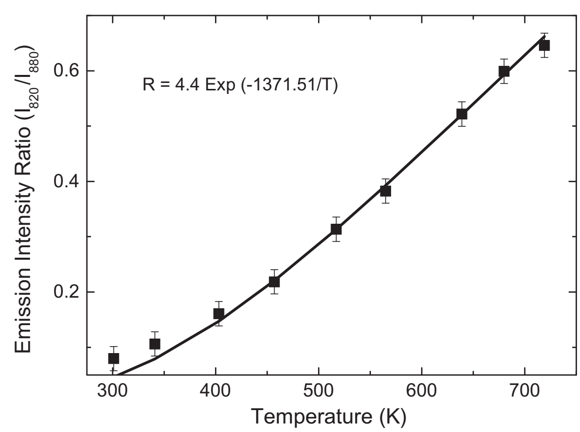

Fig. 6. Intensity ratio of the $^4F_{5/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions as a function of temperature (■). The solid line is the fit to Eq. (1).

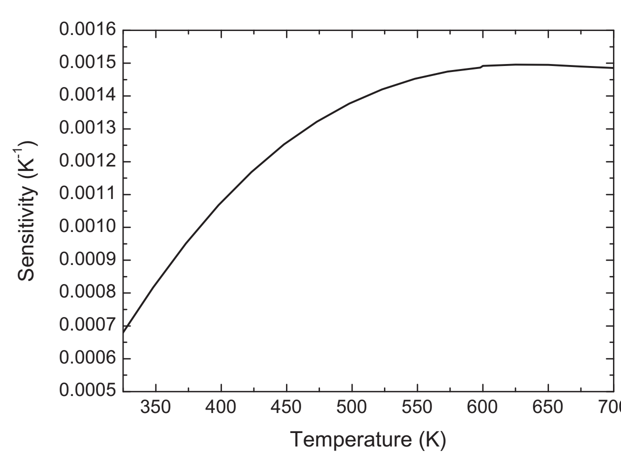

Fig. 7. The sensor sensitivity as a function of temperature of Nd^{3+} doped SBN glass ceramic.

analysis of both curves separately. From the fit values of $C = 4.4$ and $E_{32} = 953.1\ cm^{-1}$ have been found. The energy gap is in good agreement with the value obtained from the absorption spectrum ($995\ cm^{-1}$). The curve of sensitivity is defined by Eq. (2) and it is shown in Fig. 7. At 600 K, the sensitivity of Nd^{3+} doped SBN glass ceramic reached its maximum value about $0.0015\ K^{-1}$. Moreover, larger values for the sensitivity are expected at higher temperatures.

4. Conclusions

The FIR technique was carried out in Strontium Barium Niobate (SBN) glass ceramic samples to extend the knowledge of this kind of matrix. The samples were doped with Erbium and Neodymium ions (2.5 mol%). The thermalized level $^4S_{3/2}$ ($^2H_{11/2}$) of Er^{3+} ions was studied in a wide temperature range from 300 K to 700 K with a maximum sensitivity of $0.0017\ K^{-1}$ at 600 K. In the Nd^{3+} doped sample, the emission bands corresponding to the $^4F_{5/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions were analyzed as a function of temperature from 300 K to 700 K with a maximum sensitivity of $0.0015\ K^{-1}$ at 600 K. The emission bans of the thermalized levels used in this work have a weak or negligible overlap. Therefore, it is expected a lower error in application of the FIR technique using the values of the emission intensities.

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