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Analysis of Er^{3+} and Ho^{3+} codoped fluoroindate glasses as wide range temperature sensor

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ABSTRACT

The fluorescence intensity ratio technique for two fluoroindate glass samples has been carried out. The green emissions at 523 nm and at 545 nm in a 0.1 mol% of Er^{3+} doped fluoroindate glass was studied in a wide range of temperature from 125 K to 425 K with a maximum sensitivity of 0.0028 K^{-1} for 425 K. In a sample doped with 0.1 mol% of Ho^{3+} the emissions at 545 nm and at 750 nm were analyzed as a function of temperature from 20 K to 300 K obtaining a maximum sensitivity of 0.0036 K^{-1} at 59 K. Using both fluoroindate glass samples a wide temperature range from 20 K to 425 K is easily covered pumping with two low-cost diode laser at 406 nm and 473 nm.

1. Introduction

Due to their energy level structures, the rare earth (RE) ions doped materials have extensive applications in viewers and indicators, color displays, high density optical data reading and storage [1–4]. RE doped materials have received significant attention for optical temperature sensors because their absorption and emission properties as a function of the operating temperature could cause changes in the fluorescence intensity [5,6]. Fluoroindate glasses present a large potential to be used in these devices. The low multiphonon emission rates and large transparency of this matrix make them a promising material as optical temperature sensor [7–10].

The optical temperature sensors could be calibrated by fluorescence intensity ratio (FIR) technique [13]. This technique presents the advantage of reducing the influence of measurement condition and the sensitivity of the measurement improves. The technique only needs to compare the intensity of the peaks or the areas of the emissions. In both cases, the setup experiment does not require a great resolution [14]. Several researcher groups have developed their investigation in the application of FIR technique on RE doped materials [11–15].

In this paper, we present experimental results of the luminescence of two samples, one doped with Er^{3+} ions and the other one doped with Ho^{3+} ions. These samples are doped with 0.1 mol%. Using these fluoroindate glass samples a wide temperature range from 20 K to 425 K has been studied as an optical temperature sensor based on the FIR technique.

2. Experimental

Starting composition for sample preparation was in mol%: $(40 - x)$ InF_3, 20ZnF_2, 20SrF_2, 20BaF_2 and $x$$REF_3$ with $x = 0.1$ or 2.5 (where RE represents Er^{3+} or Ho^{3+} ions) [16]. The chemical analysis of the glasses has been obtained with a Dispersive X-Ray Microanalyzer (Oxford Instruments Microanalysis Group 6699 ATW). The final composition of the glasses was the same as the starting composition. The compounds were of 99.5% purity or better. The mixture of the desired composition was heated during 1 h at 675 K with NH_4FHF in order to force the conversion of residual oxide species to fluorides. After this process the mixture was melted at 1175 K. The melt was poured into aluminium mould preheated to 575 K, yielding glass plates with 1–2 mm thickness.

The emission spectra were obtained by exciting with a diode laser excitation at 406 nm and 473 nm, detecting with a 0.25 m

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monochromator and photomultiplier. The emission spectra were corrected by the system spectral response. Helium continuous flow cryostat was used for low temperature measurements in the range from 12 to 295 K. A small furnace was used to high temperature measurements in the range of 295–425 K.

3. Results and discussion

The interest in the development of rare earth doped matrix for temperature sensors has increased due to the low cost of the material fabrication and the easy pumping condition by using low-cost diode laser. In these materials many pairs of energy levels with small separation of the order of the thermal energy are known. For practical sensor, 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 FIR technique is used to calibrate the temperature sensor. 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 temperature dependent ratio of these intensities is independent of the source power intensity since the emitted intensities are proportional to the population of each level involved. This relative population between the two levels, R, follows a Boltzmann-type population distribution:

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

where K is the Boltzmann constant, E_{32} is the energy gap between these two excited levels, g_3, 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 R changes with the temperature is;

$$S = \frac{dR}{dT} = R\left(-\frac{\Delta E_{32}}{kT^2}\right) \qquad (2)$$

This expression represents the sensor sensitivity, S. From Eq. (2), it is clear that having pairs of energy levels with large energy differences increases the sensitivity. However, as the energy difference become larger, the population and the intensity from the upper of the thermalized levels will decrease and other physical processes could appear.

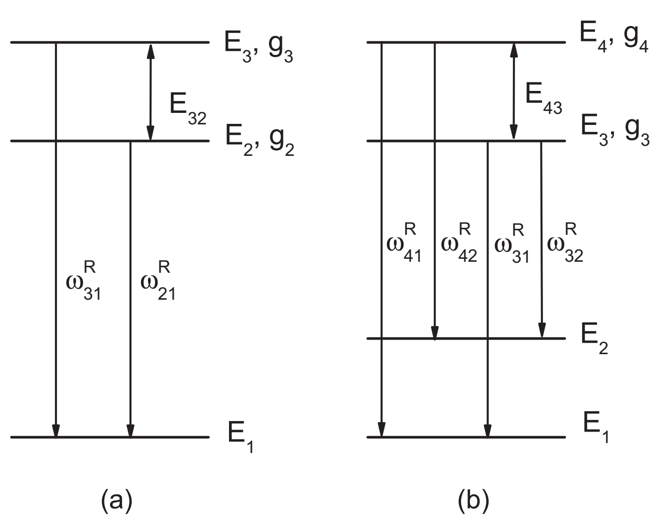

Fig. 1. Simplified diagram for (a) three and (b) four levels. E_{ij} is the energy gap between these two excited levels, g_i is the degeneracy of the i-level and ω_{ij}^{R} is the spontaneous emission rate between the i and j-level.

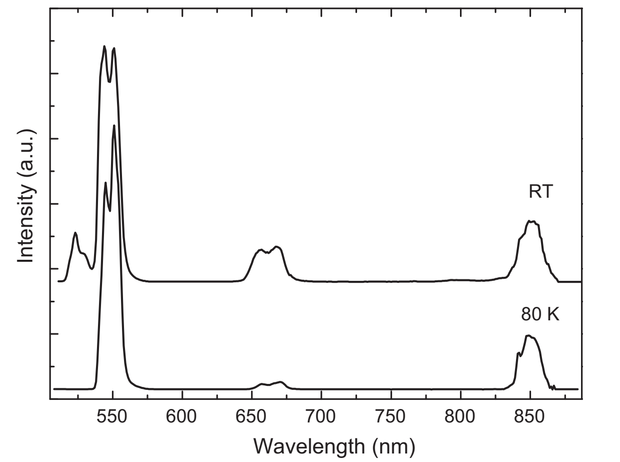

Fig. 2. Emission spectra in the visible range for 0.1 mol% Er^{3+} at 80 K and *RT* with excitation at 406 nm.

The literature indicates that there are only a few rare earth ions which can be used for sensitive temperature measurement. The most common is the case of the Erbium doped materials, which have been extensively studied as temperature sensor [12,14,15]. Berthou and Jorgensen [11] have first reported the FIR technique with thermally coupled $^2H_{11/2}$ and $^4S_{3/2}$ levels of Er^{3+} doped in fluoride hosts using either 488 nm or 970 nm excitation over the 293–473 K temperature region. Fig. 2 shows the emission spectra of the Er^{3+} doped fluoroindate sample in the visible range at room temperature (*RT*) and at 80 K. The two emission bands at 523 nm and 545 nm correspond to $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions, respectively. The positions of the two bands do not change while the temperature is increasing, whereas the FIR of these emissions is modified. The small energy gap between the two levels, which is obtained from the absorption spectrum [16] (640 cm^{-1}), allow the thermalization of $^4S_{3/2}$ ($^2H_{11/2}$) levels. An analysis based on a simple three-level system comprised of the $^2H_{11/2}$ (level 3), $^4S_{3/2}$ (level 2) and $^4I_{15/2}$ (level 1) has been carried out. The ratio between the intensities of the areas at 523 nm ($^2H_{11/2} \rightarrow {}^4I_{15/2}$) and 545 nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$) 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 125 K to 425 K for the glass sample (see Fig. 3). From the fit the values of $C = 6.8$ and $E_{32} = 861$ cm^{-1} have

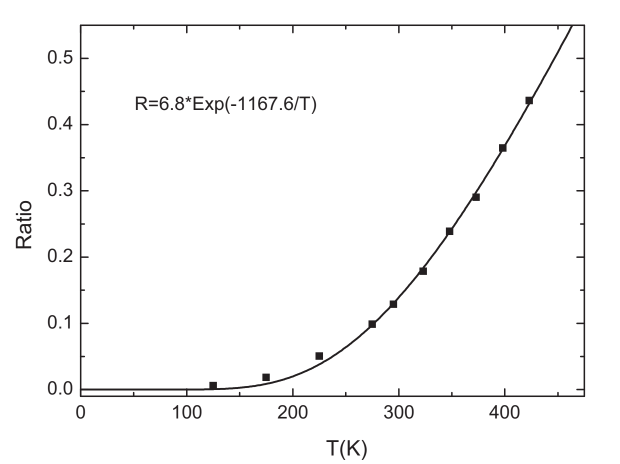

Fig. 3. Intensity ratio of the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions as a function of temperature (■). The solid line is the fit to Eq. (1).