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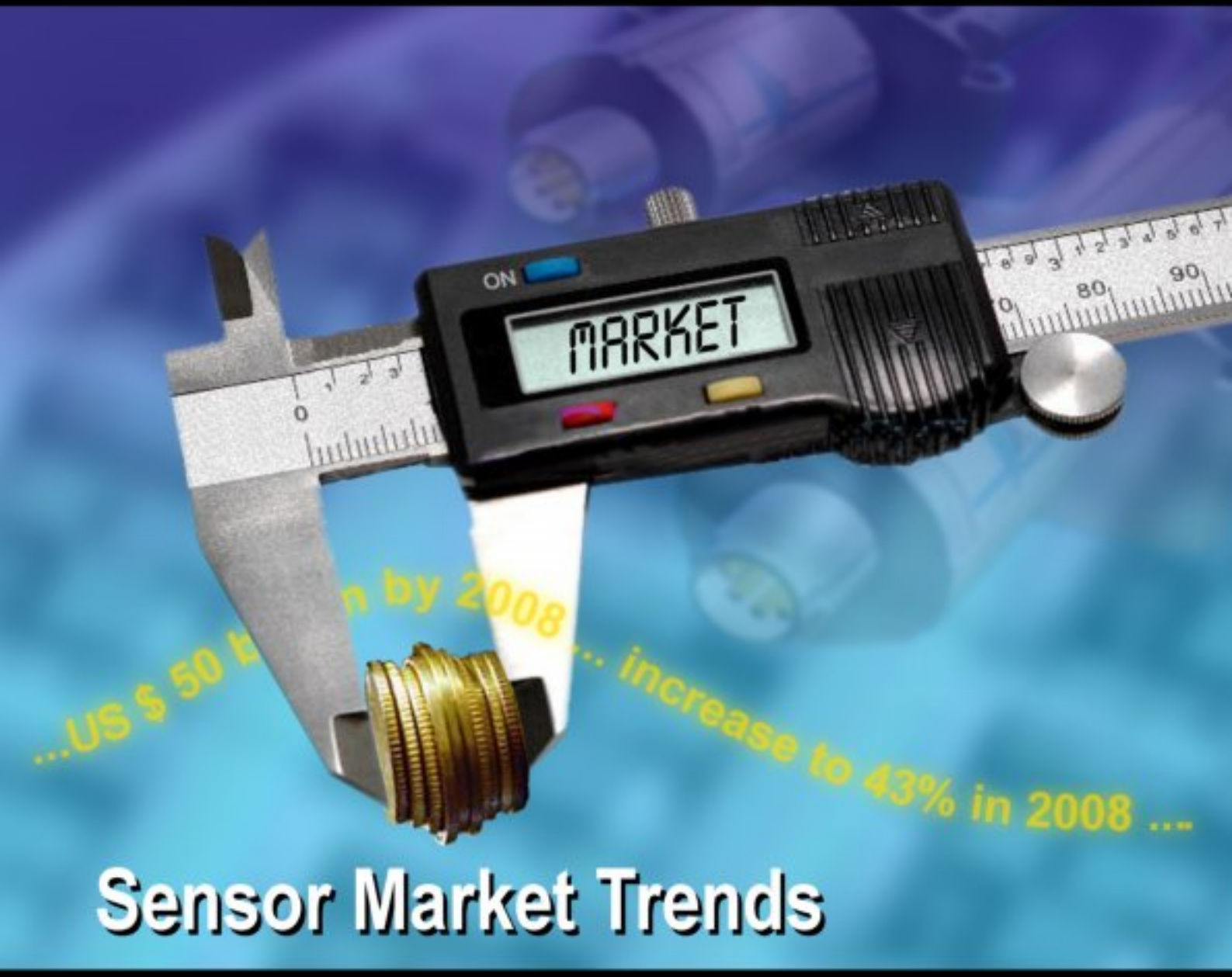

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Experimental Validation of Fluorescence Intensity Ratio /Fluorescence Lifetime Temperature Sensing Technique

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Abstract: Both the temperature sensing scheme FIR and FL has been compared on the basis of the experimentally observed data from Eu^{3+} doped calibo glass having the energy level separation (E~1725cm^{-1}) between the two $^5D_1$ and $^5D_0$ levels. On the basis of the error estimations and the sensitivity values as observed it is concluded that the FIR technique would be the better one to monitor the temperature over a wide range 298-550K temperature compared to the FL technique.

Keywords: Fluorescence lifetime; Fluorescence intensity ratio; Triply ionized europium; Sensitivity; Quantum efficiency; Upconvertors

1. Introduction

Triply ionized europium with $4f^6$ electronic configuration has a regular ^7F multiplet as its ground state followed by a ^5D multiplet as its first excited state. The second component of the ground multiplet $^7F_1$ is only ~360cm^{-1} above the ground state $^7F_0$ hence the thermal populations even at the normal room (~300K) temperature may not be ignored and due to this reason the absorption transitions arising from both the $^7F_0$ and $^7F_1$ level are seen. The transitions starting from the $^7F_0$ level are observed in the absorption spectrum at liquid nitrogen temperature [1, 2]. Triply ionized europium is one of the most widely studied rare earth ion incorporated in glassy/crystalline hosts for its radiative properties and used in many optical devices such as phosphors, upconvertors, optical fiber amplifiers etc. [3-10]. The absorption and fluorescence spectra of the europium ion are sensitive to the environment of the host and therefore, the triply ionized_europium ion can be specially used as a probe for finding the local

structure around the rare earth ion in a crystal or a glass, due to the relative simplicity of its energy level structure with a non degenerate ground state $^7F_0$ [11, 12]. Triply ionized europium embedded in optical fibers/glasses has also been utilized for monitoring the temperature with appreciable sensitivities [13-16].

2. Experimental

The chemical compositions of the calibo glasses doped with Eu^{3+} is as follows:

$$(70\text{-}x)\ H_3BO_3 + 20\ Li_2CO_3 + 10\ CaCO_3 + x\ Eu_2O_3$$

where x= 0.50, 0.75, 1.0 and 1.25 mol%

Homogeneously well mixed sample is put in a platinum crucible at 800-1000^{0}C for an hour. The melt was cooled to room temperature to get a properly annealed glass of desired shape and size. The non-crystalline behavior of these glasses has been tested through X-ray diffraction. For fluorescence measurements 476.5nm line of an Ar^+ laser with 150mW power has been used as an excitation source and the fluorescence was dispersed using a 0.5m Spex monochromator attached with a IP21 photomultiplier tube.

3. Results and Discussion

The energy level diagram for the fluorescent Eu^{3+} ion is shown in Fig 1. If the rate of relaxation between the two upper levels 2 and 1 due to the rapid thermalization is very small, the thermalized fluorescence lifetime may be given by [17] as

$$\tau = \left(\frac{1 + b_{21}}{A_{10} + A_{20} b_{21}}\right), \tag{1}$$

where A_{20} and A_{10} are the spontaneous transition rates corresponding to the two levels 2 and 1. $b_{21} = (g_2/g_1)\ exp\ (-\ddot{A}E_{21}/kT)$, is the ratio of the population in levels 2 and 1 at equilibrium. g_2 and g_1 are their respective degeneracies, k the Boltzmann's constant and T is the Kelvin temperature.

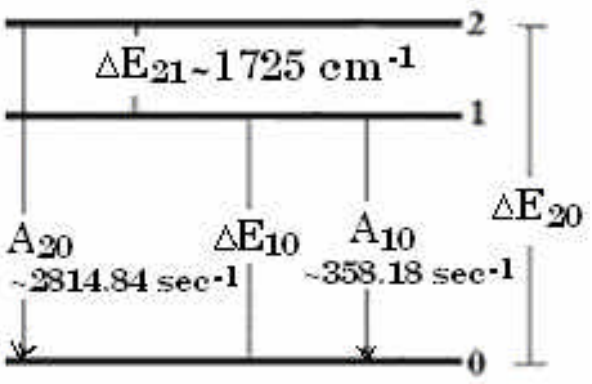

Fig. 1. Energy Level Diagram of Eu^{3+} ion.

The fluorescence intensity ratio of the two transitions resulting from the two levels 2 and 1 to the 0^{th} level can be defined as

$$FIR(R) = \frac{g_2 \sigma_{20} w_{20}}{g_1 \sigma_{10} w_{10}} e^{-\frac{\Delta E}{kT_2}} = B e^{-\frac{\Delta E}{kT_2}}, \quad (2)$$

where $B = \frac{g_2 \sigma_{20} w_{20}}{g_1 \sigma_{10} w_{10}} = 18.08$.

From equations 1 and 2 it may be visualized that both '$\hat{o}$' and 'FIR' are independent of the source intensity, which is an essential condition for any temperature monitoring scheme.

The spontaneous emission transition probabilities for the $^5D_1$ and $^5D_0$ levels of Eu^{3+} are ~2814.84sec^{-1} and ~358.18sec^{-1} respectively [18]. The resultant fluorescence lifetime at lower temperatures is noted to be approximately the same as the radiative lifetime of the $^5D_0$ level. The resultant fluorescence lifetime at room temperature (300K) is calculated using equation (1) and the value thus obtained is ~2.66ms. The lifetime of D_0 level at different temperatures monitored and found that they decrease with increasing temperature caused by the increased non-radiative relaxation rates.

One considers '$\hat{o} / \hat{o}_1$' {the ratio of the thermalized lifetime '$\hat{o}$' from equation (1) to the lifetime ($\hat{o}_1$) of the lower ($^5D_0$) level} in the fluorescence lifetime method and a plot of the same i.e. $\hat{o} / \hat{o}_1$ versus temperature is shown in Fig 2. It is observed that the theoretical and the experimental values differ by not more than ~20%.

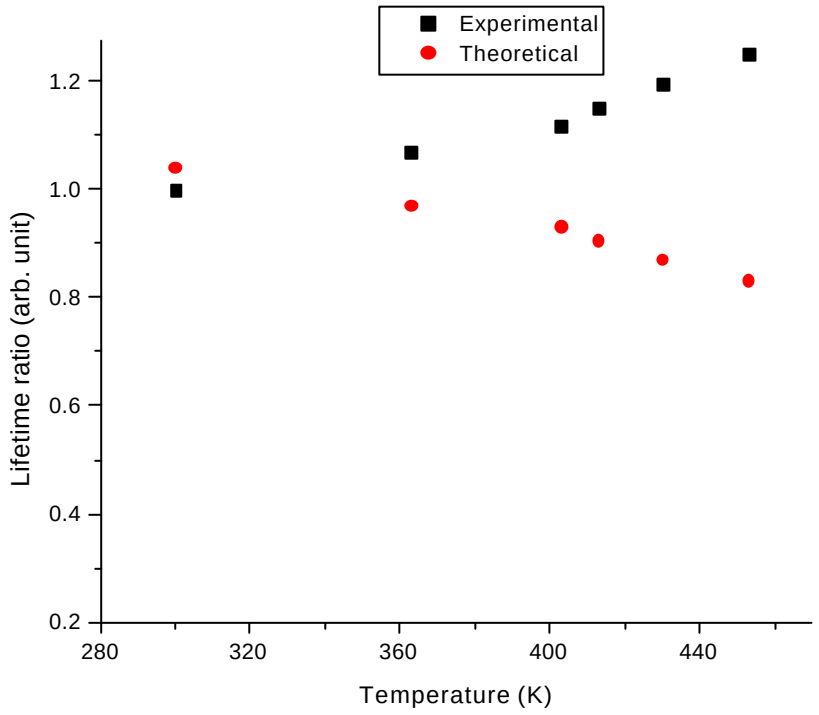

Fig.2. Variation of lifetime ratio with temperature.

The variation of the FIR with temperature is shown in Fig 3. The difference between the experimental and the theoretical values is not more than ~6.05% for the given temperature range. It is observed from Fig 2 and Fig 3 that the variations with temperature for the two methods are much different. It is also necessary to compare the sensitivities S for the two techniques:

1) The sensitivity of the fluorescence lifetime may be given as

$$S_s = \frac{1}{t}\frac{\partial t}{\partial T} = \left(1 - \frac{1}{1+b_{21}}\right)\left(\frac{1-\frac{A_{20}}{A_{10}}}{1+\frac{A_{20}}{A_{10}}b_{21}}\right)\frac{\Delta E_{21}}{kT^2} \tag{3}$$

2) Sensitivity (*S*) of the Fluorescence intensity ratio can be obtained from

$$S = \frac{1}{R}\frac{\partial R}{\partial T} = \frac{\Delta E_{21}}{kT^2} \tag{4}$$

The quantum efficiency may be given as

$$\varsigma = \frac{t_{exp}}{t_{rad}} \tag{5}$$

The values for $\hat{o}_{exp}$ and $\hat{o}_{rad}$ for 1.0mol% Eu^{3+} doped calibo glass are 1.04 ms and 2.79 ms respectively [18]. The quantum efficiency for the present case is observed to be ~ 37 %.

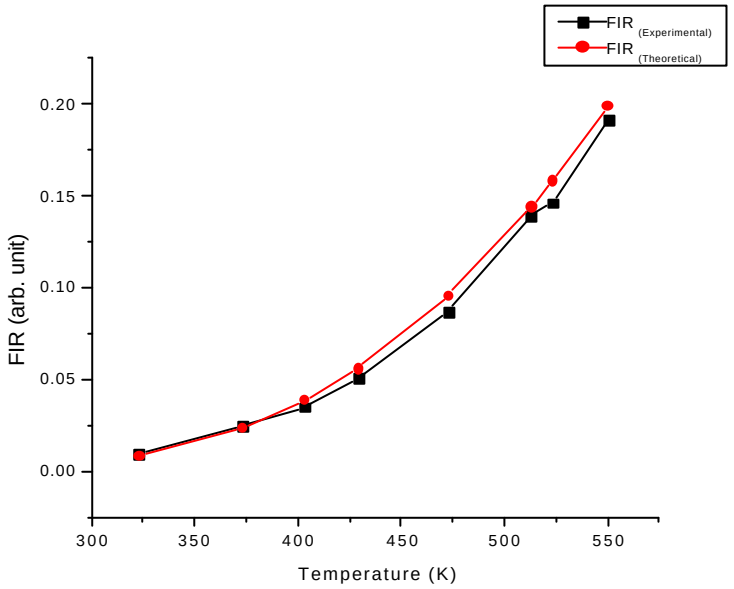

Fig. 3. Variation of FIR with temperature.

The sensitivities of both the techniques using equations 3 and 4 have been calculated and are noted to be ~0.01448 %/K and ~2.75 %/K at room temperature (300K) respectively. Thus, it is clear that though both techniques may be used to monitor the temperature but for higher temperature region (i.e. >400K) the FIR technique would be superior compared to the FL technique.

4. Conclusions

Sensing behavior of both the techniques has been compared on the basis of the experimentally observed data. It is found that the fluorescence intensity ratio technique for the present system (with quantum efficiency ~37%) can be used to monitor the temperature for low as well higher temperature region with high precision compared to the fluorescence lifetime.

Acknowledgements

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