

Ho³⁺:TeO₂ glass, a probe for temperature measurements

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Abstract

Considerable effort has recently been devoted to the development of optical fiber based temperature monitoring device owing to their advantage over conventional thermometric techniques. Optical thermometry based upon near infrared excited upconversion fluorescence emission in Ho³⁺ activated tellurite glasses excited at 890 nm is presented. Temperature sensing in the range 265–440 K within 2 K accuracy using excitation powers readily obtainable from commercially available Ti–sapphire laser have been achieved. This temperature sensing approach is independent of fluctuations in excitation intensity, environment, transmission and requires a simple and low cost signal detection and processing system. Our results also indicate that the glassy host material also plays a major role in the process of the temperature sensing capacity.

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1. Introduction

Recently we have studied the optical properties and upconversions in Ho³⁺ doped in tellurite glass [1]. TeO₂ as host material has several advantages over other oxide glass hosts the most important being its low phonon frequency [2]. Its good mechanical strength and chemical durability, low processing temperature and excellent transmission in the visible and near IR up to 4.5 μm are other advantages making tellurite glasses a good candidate for the development of glass optical devices [3–5]. Rare earth doped these glasses were also found suitable for temperature sensing. In this paper we propose a sensor, based on Ho³⁺ doped tellurite glass upconversion fluorescence, that should offer the advantages since their absorption and emission properties are temperature dependent [1]. This behavior is due to the broadening of the homogeneous line width and to the changing population of the energy sublevels with temperature. Rare earth doped glass have already been investigated for the sensor development of point. Rai et al. [6] have presented an investigation of possible application of yellow intensity ratio of Pr³⁺ doped tellurite glass to high dynamic range temperature sens-

ing. Thus Tripathi et al. [7] have presented energy transfer based upconversion temperature sensor based on fluorescence intensity ratio technique. Kusama et al. [8] for the first time discussed the fluorescence intensity ratio techniques for temperature monitoring using Y₂O₂S:Eu phosphor as the sensing medium within 100–300 K temperature range. The effect of temperature on the fluorescence from ⁵D₁ and ⁵D₀ levels using Eu³⁺ doped optical fiber with 465 nm line as an excitation source have been investigated [9]. The main drive of this investigation has been to produce a range of fluorescence intensity ratio based technique which can be used for a variety of different sensor purpose, providing a foundation for an effective measurement technology which can complete with conventional method in niche area. Therein lies recipe for the success of optical fiber sensors in tackling difficult measurement situations where conventional sensors are not well suited to use in a particular environment. The resulting sensors have a series of characteristics that are familiar that they are compact and light weight, in general minimally invasive and these sensors offer the prospect that they can be multiplexed effectively on a single fiber network. However, all should be immune to electromagnetic interference as there are no electrical currents flowing at the sensing point. There is, however the expectation that they should be able to be produced at relatively low competitive cost. Our results are presented in the following sections.

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2. Experimental

The glasses used in this work were synthesized by a conventional melt and quenching method described in our earlier paper [1]. The starting materials were TeO_2 , Li_2CO_3 , $\text{BaCO}_3/\text{PbO}_2$ with a purity of 99.9% and Ho_2O_3 of 99.99% purity were used. The compositions of different glasses are:

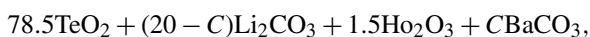


$$x = 0.5, 1.0, 1.5, 2.0 \text{ mol\%}$$

We have also prepared glasses with PbO_2 and BaCO_3 as modifiers. The compositions of different glasses are



$$B = 2.0, 4.0, 6.0, 6.5, 7.0 \text{ mol\%}$$



$$C = 10, 20 \text{ mol\%}$$



$$D = 10, 20, 25 \text{ mol\%}$$

The glasses thus obtained were annealed carefully and then were cut and polished in order to obtain samples suitable for optical measurements. The refractive index of the glasses was measured by polarization dependent Brewster angle measurements at 632.9 nm. The density of the glass was measured using conventional Archimedes principle with xylene as an immersion liquid and a single pan electric balance.

The upconverted fluorescence spectra in the range of 300–700 nm was excited using 890 nm line from a $\text{Ti}:\text{Al}_2\text{O}_3$ laser pumped by second harmonic of $\text{Nd}:\text{YVO}_4$ laser and recorded using a 0.5 m Spex monochromator attached with IP21 photomultiplier tube. The spectra were recorded using a double pen chart recorder. For temperature dependent fluorescence measurements the sample was heated in a home made furnace attached with a thermocouple. NIR radiation of wavelength 890 nm from $\text{Ti}:\text{Al}_2\text{O}_3$ laser was also used to excite upconversion emissions and for measuring the life time of the $^5\text{F}_4$ ($^5\text{S}_2$) level.

3. Result and discussion

The fluorescence spectra of Ho^{3+} doped in the TeO_2 lattice have been monitored for different concentration of Ho^{3+} . The fluorescence yield is maximum for 1.5 mol% of Ho^{3+} . Fig. 1 shows the fluorescence spectrum of 0.5, 1.0, 1.5 and 1.7 mol% Ho^{3+} doped glass between 300 and 700 nm regions at room temperature using 890 nm line of $\text{Ti}:\text{Al}_2\text{O}_3$ laser. The intensity of Ho^{3+} upconversion bands increases up to 1.5 mol% of Ho^{3+} and decreases for higher concentrations. This decrease is due to self-quenching of the fluorescence via exchange or ion pair relaxation mechanism in glasses at higher concentrations of the rare earth.

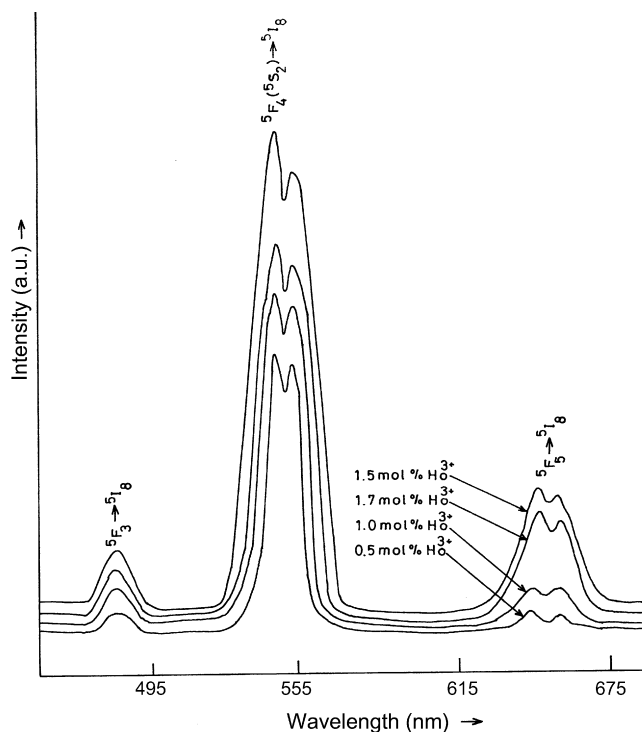


Fig. 1. Upconverted fluorescence spectrum of $\text{Ho}^{3+}:\text{TeO}_2$ glass at 980 nm excitation.

The average interatomic separation between the two ions ($\text{Ho}^{3+}:\text{Ho}^{3+}$) for 1.5 mol% of Ho^{3+} doped glasses have also been calculated using the formula [10]

$$\text{interatomic separation} = (\text{total rare earth ion concentration})^{-1/3}$$

This interatomic separation at 1.5 mol% concentration is ~ 1.9 nm (much larger than the sum of radii of two ions), which indicates that rare earth ions interact themselves and transfer their excitation energy from one ion to other via multipolar interaction. The enhanced nonradiative coupling results in a decrease in the fluorescence efficiency. The small energy separation between the two levels ($^5\text{F}_4$ and $^5\text{S}_2$) of Ho^{3+} indicates that they are thermally coupled to each other also and population in the two levels at a fixed concentration will depend on the temperature of the glass. This temperature dependence could arise either due to energy transfer or by multiphonon relaxation. The fluorescence emission lifetime is given as

$$\frac{1}{\tau} = W_R + W_{MP} + W_{CR} + W_{ETU} \quad (1)$$

where τ is the lifetime of the level and W_R , W_{MP} , W_{CR} and W_{ETU} are the radiative transition probability of energy transfer, multiphonon relaxation, cross relaxation and energy transfer upconversion respectively. At low concentration W_{ETU} and W_{CR} are negligibly small and can be neglected. As the temperature is raised (at a fixed concentration) the multiphonon relaxation increases and play dominant role in reducing the population and thereby the fluorescence intensities of the bands. The nonradiative decay rate at room temperature (28 °C) is found to be $7.85 \times 10^2 \text{ s}^{-1}$.

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