Sensors and Actuators A 233 (2015) 324–329

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Optical temperature sensing using a new thermographic phosphor

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ARTICLE INFO

Article history:
Received 11 May 2015
Received in revised form 11 July 2015
Accepted 11 July 2015
Available online 26 July 2015

Keywords:
Phosphor
Optical sensor
Temperature sensor
Luminescence

ABSTRACT

The luminescence emission of a new thermographic phosphor based on Chromium(III)-doped yttrium aluminum borate (Cr^{3+}:YAB) has a strong temperature dependence, which makes this material well suited for temperature sensing. In this work the luminescence emission decay was investigated in great detail in a broad temperature range, both in time and frequency domain. The results obtained with these two measuring techniques, which are consistent, are used to determine the optimal design parameters for sensor development. The high sensitivity which is thus achievable, together with the high stability of the material, demonstrate that this phosphor is very suitable for the design of a sensitive, low-cost, and robust contactless temperature sensor. Due to the insensitivity of the sensing properties to the immobilization matrix, this material can be easily incorporated in the most appropriate matrix depending on the application.

1. Introduction

The optical measurement of the temperature is of great interest for applications which include, among others, biological imaging, medicine, environmental monitoring, industrial process control and chemical industry [1]. The several advantages of optical sensing include being contactless, not needing electrical connections, and insensitive to magnetic fields. Additionally, since the typical sensor can be as small as the optical fiber itself, optical readout allows non-invasive, in situ and, due to the small thermal mass, also very rapid thermal detection. The interest in temperature measurement is not only limited to the determination of the temperature itself. Indeed, temperature is needed for compensation during optical sensing of many analytes such as oxygen, pH or CO_2. For example, temperature is important in optical sensing of oxygen since quenching by oxygen is strongly temperature dependent [2].

Because of the large number of temperature-dependent optical properties, several approaches to optical temperature sensing have been investigated in the last years [1,3–5]. Among these, a promising approach is the use of luminescent materials and the detection of the temperature-dependent intensity decay. This approach has been implemented through different optical fiber sensing schemes: using the fiber itself as the sensing element, for example single-crystal ruby fibers [6]; those with the luminescent material attached to the tip of a fiber [7,8] and schemes for remote sensing, with the material detached from the fiber, either embedded in an optode [9] or coated on the surface whose temperature must be measured [10–12]. In this work it will be shown that the thermographic phosphor investigated is well suited for both of the latter two schemes.

Although virtually all luminescent materials are expected to show a temperature dependence of the luminescence intensity or of the luminescence intensity decay time, some indicators show stronger thermal effects, making them better suited for practical applications. Depending on the temperature range, the required sensitivity and stability, several classes of luminescent materials have been proposed in the past years. Some examples, to cite only a few, are magnesium fluorogermanate Mn(IV) [13,14], ruby [15], alexandrite [16], Y_2O_3:Eu [12], Ru-phen complexes [17,18], rare-earth phosphors [19,20] and Europium complexes [21–23]. Furthermore, doping with transition-metal ions, for example Cr^{3+}, allows one to achieve a wide absorption spectrum and to tune the desired thermometric properties thanks to strong crystal field interactions. A comprehensive review of the luminescence probes and sensors has been published recently [24].

Particularly for temperatures which are relevant for biological imaging, medicine, environmental monitoring and biopharma applications, a new promising indicator is Chromium(III)-doped yttrium aluminum borate $YAl_3(BO_3)_4$:Cr^{3+} (Cr^{3+}:YAB) [25]. This material is characterized by a broad excitation range in the visible,

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http://dx.doi.org/10.1016/j.sna.2015.07.009
0924-4247/

a near-infrared (NIR) emission and a high luminescence brightness, which is characteristic of many Cr^{3+}-doped indicators.

In this work the thermometric properties of Cr^{3+}:YAB are fully characterized in a broad temperature range. The achievable sensitivity is determined for the two most common detection schemes, in time and frequency domain. After comparing the results, the implications for the design of a sensor are discussed and the optimization parameters for practical implementation determined. Finally the robustness of this material is demonstrated, showing how Cr^{3+}:YAB can be used to make an inexpensive, robust but at the same time sensitive temperature sensor.

2. Experimental

2.1. Sample preparation

The Cr^{3+}:YAB microcrystalline powders were prepared as described in [25] and further milled down to obtain crystals with maximal size of few hundred μm (Fig. 1). The samples were not milled further to avoid reduction of the response time due to increased surface defects. Slightly higher decay times are expected when using single crystals because of the reduced number of impurities of the yttrium borate and of inner defects in the crystal structure. To analyze these materials the ground powder crystals were immobilized in polyester (Bayer Desmophen 670) to achieve a film of approximately 0.5 mm. The choice of the material was due to the good spin coating fluidity, which allowed us to realize thick films and to achieve high emission intensities.

To investigate the dependence of the florescence emission on the matrix material, a second set of samples was prepared immobilizing the microcrystals in silicone rubber (Wacker Elastosil RT 601). The use of silicone rubber as matrix allows the realization of semi-transparent thin films with a thickness of approximately 100 μm.

2.2. Experimental setup

For the measurements in the lower temperature range, between 0 °C and 80 °C, the samples were placed in good thermal contact with a Cu-plate. The temperature of this plate was varied using a Peltier element and stabilized with a temperature controller (PTC10, Stanford Research Inc.). For temperatures above 80 °C the Peltier was substituted by a resistive heating element. The entire setup, composed of sample holder and heating element, was thermally insulated from the ambient air to reach the maximum temperature of 200 °C.

Although a number of sensor system designs are based on the measurement of the fluorescence intensity, thermometric techniques based on measuring the intensity decay time have shown higher reliability and robustness [26], being therefore preferable for practical applications. The decay time can be either directly measured or determined through the phase-shift method in the frequency domain. In this work Cr^{3+}:YAB was investigated using both approaches.

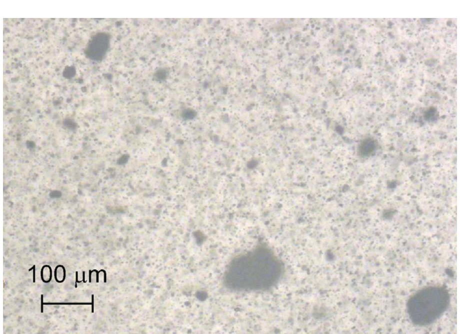

Fig. 1. Microscopic image of the Cr^{3+}:YAB microcrystalline powder immobilized in silicone rubber.

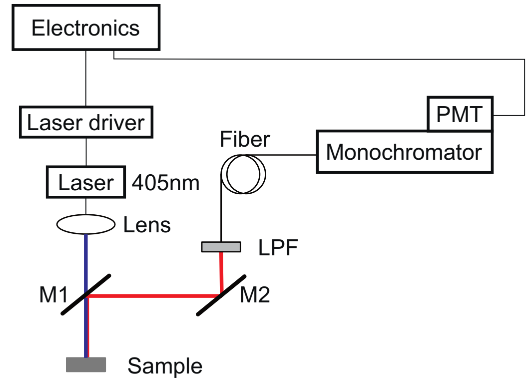

Fig. 2. Scheme of the optical experimental setup. M1, M2: parabolic mirrors; LPF: low pass filter; PMT: photomultiplier.

The luminescence intensity decay times were measured using the technique of time-correlated-single-photon-counting (TCSPC). Compared to the direct record of the intensity decay profile after one single excitation pulse, for example with fast photo diodes, where very high intensities are required, TCSPC achieves data collection over multiple excitation–emission cycles and reconstructs the decay profile from many events collected over the cycles. This allows a very high resolution of the intensity decay curve.

The optical setup used in this work is shown in Fig. 2. The excitation light was provided by a 405 nm laser diode (Sanyo DL-5146) focussed on the surface of the samples with a collimation lens (ThorLabs C671TME-405). The fluorescence was collected using two off-axis parabolic mirrors (Edmund Optics). A hole was drilled in the first mirror for the throughput of the excitation laser light. To suppress excitation light reflected by the sample surface, the emission channel was equipped with an OD5 long pass filter with cut-off at 594 nm (Semrock 594 LP Edge Basic Langpass). The light collected by a fiber bundle was then analyzed using a monochromator (Bruker 250sm/is) and then collected by a photomultiplier (Hamamatsu H10721-01). The excitation pulse was generated by a frequency generator (Agilent 33220A) which sent the synchronization signal to the acquisition electronics (Time Harp Picoquant 260). The duration of the pulses was typically between 500 ns and 1 μs, since the decay times to measure are between 100 and 200 μs. The duration of the pulses as well as the intensity of the laser were adjusted to maximize the signal-to-noise ratio, avoiding however "pile-up" effects [26]. The instrument response function (IRF) was measured with a diffusing quartz plate and was established to be much shorter than the measured luminescence decay times. Therefore no mathematical analysis of the convolution between the IRS and the real fluorescence signal was necessary.

The optical setup was only slightly modified for the phase-shift measurements. For the frequency generation and the phase detection a two-phase lock-in amplifier (SR830, Stanford Research Inc.) was used. The modulation frequency was varied between 200 Hz and 5 kHz.

3. Results and discussion

The normalized luminescence intensity decay for six temperatures between 5 °C and 180 °C is shown in Fig. 3. The intensities are plotted normalized to display better the changes with the