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Optical differential temperature measurement with beat frequency phase-fluorometry

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Abstract

We present a new method for differential temperature measurement based on thermal sensitivity of the fluorescence lifetime of thermographic phosphors (TP). Pairs of thermographic phosphors are excited with intensity modulated light at frequencies ω and $\omega + \omega$. The phase shift θ of the summary fluorescence intensity beat signal envelope is measured. A prototype of fluorometric differential temperature sensor is developed and feasibility of the method is experimentally demonstrated with a $\text{Sm}^{2+}:\text{SrFCl}$ crystal and the $^5\text{D}_1 \rightarrow ^7\text{F}_0$ transition for high thermal sensitivity. The observed linear dependence between envelope phase shift θ and temperature difference T agrees with the theoretical prediction. Sensitivity of $S = -0.97^\circ/\text{C}$ was achieved. This method could also be applied to differential measurements of any parameter affecting fluorescence lifetime.

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(280.6780) Remote sensing and sensors; (160.2540) Temperature; (300.6470) Fluorescent and luminescent materials

1. Introduction

Optical temperature sensors, based on thermographic phosphors' luminescence dependence on temperature, have been studied for several decades, and many temperature measurement approaches have been invented and characterized [1]. They can be divided into two main groups: time-integrated and time-resolved methods [2].

Time-integrated methods exploit the temperature dependence of emission spectra. Direct measurement of luminescence intensity is the simplest implementation, but it suffers from

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the addition of noise due to instabilities of the excitation light source and detection system [3, 4]. Nevertheless, for some materials, this method may have a formidable operation temperature range from 123–873 K [5]. By contrast, the more complex fluorescence intensity ratio (FIR) method usually has a narrower range [6, 7], but is independent of spectral losses, external interferences, and fluctuations in the excitation density. The FIR method is based on calculation of the ratio between intensities of thermally coupled fluorescence maxima related to a single fluorophore [8] or multiple fluorophores [9].

The time-resolved methods rely on the known dependence of emission lifetime on temperature [10]. In contrast to intensity, this is an absolute measured quantity, which permits temperature sensors free of the need for frequent recalibration. There are two potential implementations: 1) intensity temporal decay is measured after an excitation pulse or 2) the phase shift of luminescence is recorded with respect to periodically modulated excitation, i.e. phase fluorometry [11].

Importantly, sensitivity is influenced not only by the method choice, but also by the choice of luminescent medium, and many different materials have been studied as possible temperature sensing media including organic dyes [12], polymers [13], layered double hydroxides [14], quantum dots [15] and phosphors such as rare-earth-doped crystals [16]. The latter have enabled the greatest sensitivity over wide temperature ranges by virtue of great material stability.

While the ability to optically measure single temperatures is well developed, many applications require differential temperature measurements. Examples include calorimetric sensors [17], thermal balance in industrial processes [18], and medical applications including heart rate measurements [19], as well as detection [20] and treatment [21, 22] of cancer. In all these cases, use of two separate sensors or two consecutive measurements may introduce additional systematic errors (biases, offsets, drifts) caused by the analog light-to-photocurrent conversion or additive noise from temporal fluctuations. Therefore, a single-sensor differential thermometer would allow more accurate measurements.

Here we present a method for sensitive differential temperature measurement with beat frequency phase-fluorometry using a well-characterized phosphor, the rare-earth-doped crystal $\text{Sm}^{2+}:\text{SrFCl}$ [23, 24].

2. Theory

A. Dependence of fluorescence beat phase on temperature difference between two probes

In phase-fluorometric temperature sensing, the fluorescence signal, excited by an intensity modulated light source at a fixed frequency ω , develops a phase-shift θ with respect to the excitation. The intensities of exciting and emitted light can be given by the equations

$$I_{ex} = I_{ex0}[1 + a \cos(\omega t)] \quad (1)$$

and

$$I_{fl} = I_{fl0}[1 + b \cos(\omega t - \theta)] \quad (2)$$

respectively, where I_{ex0} and I_{fl} are average intensities, and a and b are the modulation amplitudes of excitation and fluorescence intensity, respectively.

In the case of single exponential decay of fluorescence, the signal phase-shift θ and its modulation amplitude b are determined by the equations [25]

$$\tan(\theta) = \omega\tau \quad (3)$$

and

$$b = a \cos(\theta) = \frac{a}{\sqrt{1 + (\omega\tau)^2}} \quad (4)$$

where $\tau = \tau(T)$ is lifetime, which in the case of rare-earth-doped solids is a temperature dependent quantity because of electron-phonon coupling, ionization, crossover relaxation and other phenomena that lead to non-radiative decay processes.

In differential temperature sensing, the main goal is to measure the temperature difference between two bodies. The straightforward way is to use two sensors measuring two phase-shifts θ , then calculate the difference of temperature values derived from equation (3) and the inverse function of $\tau(T)$. We demonstrate a more elegant direct approach, which uses two temperature probes but only a single fluorescence detector, allowing more precise differential temperature measurement by eliminating systematic errors (biases, offsets, drifts) of the analog light-to-photocurrent conversion and amplification unit. In addition, the method automatically down-converts the measurement frequency (optical heterodyning), an advantage that has been previously introduced in a cross-correlation phase fluorometry [26]. The difference of our method is that the two signals with close frequencies are added rather than multiplied.

We consider the case where two temperature probes are excited by two light sources, which are modulated at slightly different frequencies, ω_1 and ω_2 . If a single light detector operating in the linear regime collects the fluorescence emissions from these two probes, then the total photovoltage U elicited in the light detector is proportional to the sum of individual fluorescence intensities. The signal is accordingly

$$U = U_1[1 + b_1 \cos(\omega_1 t - \theta_1)] + U_2[1 + b_2 \cos(\omega_2 t - \theta_2)] \quad (5)$$

where

$$\tan(\theta_i) = \omega_i \tau(T_i), \quad i = 1, 2 \quad (6)$$

U_i is the photovoltage due to fluorescence intensity I_i , $\tau(T_i)$ is the lifetime of the luminescent material at temperature T_i and b_i is modulation amplitude.

If the two modulation frequencies are close so that $\omega_i \gg \omega$, $i = 1, 2$, then the total signal (5) will beat at the difference frequency $\omega = \omega_1 - \omega_2$ (see Fig. 1). Instead of analyzing the complex beating signal, one can extract and analyze its envelope. The demodulation of the signal can be achieved by subtracting the constant part of the signal, rectification, and finally, envelope detection (see Fig. 1). After rectification, the signal is given by

$$U_{rect} = |U_1' \cos(\omega_1 t - \theta_1) + U_2' \cos(\omega_2 t - \theta_2)| \quad (7)$$

and the envelope signal V is given by

$$V = \sqrt{(U_1' - U_2')^2 + 4U_1' U_2' \cos^2\left(\frac{\Delta\omega}{2}t - \frac{\Delta\theta}{2}\right)} \quad (8)$$

where $U_i' = U_i b_i$, $i = 1, 2$ and $\theta = \theta_1 - \theta_2$. In particular, if $U_1' = U_2' = U$, then $V = \left|2U' \cos\left(\frac{\Delta\omega}{2}t - \frac{\Delta\theta}{2}\right)\right|$.

The phase-shift of the envelope signal is θ (twice $\theta/2$, due to halving of the period by rectification). This can be directly related to the difference of two lifetimes, and therefore, to the temperature difference of two probes. In the case of relatively small differences it follows from equation (6) that

$$\frac{d(\tan(\theta))}{d\theta} \Delta\theta = \omega \Delta\tau + \tau \Delta\omega \quad (9)$$

Evaluating the derivative $d(\tan(\theta))/d\theta$ and using a relation $\tau = (d\tau/dT) T$, the following equation for small temperature difference can be derived.

$$\Delta T = \frac{1 + (\omega\tau)^2}{\omega \frac{d\tau}{dT}} \Delta\theta - \frac{\tau}{\omega \frac{d\tau}{dT}} \Delta\omega \quad (10)$$

When ω , ω and τ are known, it is possible to determine the temperature difference between two fluorescent probes by measuring θ of the envelope signal.

The sensitivity of the differential temperature measurement $S = d(\theta)/d(T)$ is given by

$$S = \frac{\omega \frac{d\tau}{dT}}{1 + (\omega\tau)^2} \quad (11)$$

This function has a maximal value at a frequency $\omega=1/\tau$, which means that the frequency always can be optimized if the average temperature is known.

In the event of large temperature differences between the measured objects, τ_1 and τ_2 might be very different. However, equation (11) will still accurately describe the sensitivity of the method. If T_1 and therefore θ_1 are fixed, then changes in T and θ will remain

proportional to change in T_2 and θ_2 . Therefore, the sensitivity $S = \frac{d(\Delta\theta)}{d(\Delta T)} = \frac{d(\theta_2)}{d(T_2)}$ follows from equation (6):

$$S = \frac{d(\arctan(\omega_2 \tau(T_2)))}{d(T_2)} = \frac{\omega_2 \frac{d\tau}{dT}}{1 + (\omega_2 \tau(T_2))^2} \quad (12)$$

From this, it also follows that the sensitivity of the beat frequency method is the same as would be achieved with two independently calibrated detectors for phase fluorometry.

B. $\text{Sm}^{2+}:\text{SrFCl}$ as a temperature sensing medium

The thermal quenching of the $4f^6$ excited states of $\text{Sm}^{2+}:\text{SrFCl}$ has been thoroughly studied in Ref. [24]. In general, the decay rate of the 5D_i , $i = 0, 1, 2$ states is a superposition of 3 terms:

- radiative decay rate (independent of temperature; in the case of the 5D_1 state this dominates below ≈ 60 K),
- non-radiative $^5D_i \rightarrow ^5D_j$ multiphonon decay rate (in the case of the 5D_1 state this dominates between $\approx 60 - 240$ K);
- non-radiative decay rate through the lowest $4f^5 5d$ state (in the case of the 5D_1 state, this dominates above ≈ 240 K).

When a differential temperature sensing in a wide temperature range is of interest, the corresponding equations and parameters published in Ref. [24] can be used for the function $\tau(T)$ and for calculating the derivative in the equation (10). However, within a limited temperature range around and above room temperature, the lifetime of the 5D_1 level can be empirically approximated by a single exponent

$$\tau(T) = \tau_0 \exp\left(-\frac{T}{T_0}\right) \quad (13)$$

where T is the temperature in degrees Celsius and the values of two constants derived from exponential fit (Fig. 2) in the temperature range of $10 - 110^\circ\text{C}$ are $\tau_0 = \tau(0^\circ\text{C}) = 143 \mu\text{s}$ and $T_0 = 29.4^\circ\text{C}$. The sensitivity follows from (11) and (13) as:

$$S = \frac{-1}{T_0} \cdot \frac{360}{2\pi} \frac{\omega\tau}{1 + (\omega\tau)^2} \quad (14)$$

At the optimal frequency $\omega = 1/\tau$, this yields $S = \frac{-1}{T_0} \cdot \frac{360}{2\pi}$. Similarly, the equation (10) can be written as

$$\frac{\Delta T}{T_0} = \frac{\Delta\omega}{\omega} - \frac{1 + (\omega\tau)^2}{\omega\tau} \Delta\theta \quad (15)$$

and,

$$\Delta\theta \approx \frac{\Delta\omega}{2\omega} - 0.017\Delta T \quad (16)$$

upon insertion of constant values and application of optimal frequency $\omega = 1/\tau$. In this case, the phase change measured in degrees has almost one-to-one correspondence with temperature. For example, $T = 0.01^\circ\text{C}$ gives $\theta = 1.7 \cdot 10^{-4} \text{ rad} \approx 0.01 \text{ deg}$ or

$$\Delta\theta \approx \frac{\Delta\omega}{2\omega} - 1 \cdot \Delta T \quad (17)$$

3. Experimental designs

A. Sensor prototype

To confirm the above described theoretical conclusion, a new optical device was developed (Fig. 3.). We used two similarly sized $\text{Sm}^{2+}:\text{SrFCl}$ crystals as temperature sensing media. The single crystals with samarium concentration of 0.3% (atomic weight units) were grown in University of Geneva by the Czochralski method in an ultrapure argon gas atmosphere. They were 0.5 mm thick and had area of 4 mm². Crystals were attached to SMA optical fiber adaptor by Faber-Castell removable adhesive and were oriented with the crystallographic (C4) axis parallel to the direction of the light beam. Their absorption spectrum range is $< 300 - 550 \text{ nm}$ and emission has multiple maxima corresponding to different $^5D_i \rightarrow ^7F_j$ transitions. We selected the maximum at 632.33 nm that corresponds to the $^5D_1 \rightarrow ^7F_0$ transition (Fig. 2).

Other system optical components were selected according to this transition. We used two Roithner LaserTechnik VL410-5-15 LEDs with emission maximum around 410 nm and FWHM of 15 nm for separate excitation of the two crystals with lights modulated at slightly different frequencies. LEDs were arranged 90 degrees relative to each other. Excitation light was directed through an Edmund Optics quartz Ø10mm spherical lens from two orthogonal directions through optical glass filters and Eksma Optics' dichroic mirrors. The transmission range was 320 – 520 nm for the optical filters and 350 – 550 nm for the dichroic filters, which reflected light in the range 625 – 725 nm.

Excitation light was focused by the spherical lens onto two quartz optical fibers, which guided excitation light onto the $\text{Sm}^{2+}:\text{SrFCl}$ crystals and collected fluorescence back to the spherical lens. The collimated fluorescence passed through dichroic mirrors that reflected light through Andover 630FS10–12.5 fluorescence interference filters (Fig. 2) onto a silicon photodiode.

Everything was assembled in a black box made from anodized aluminum. LED and photodiode contacts were made externally accessible to modulate current and perform a signal readout.

B. Generation and processing of the signals

Excitation waveforms were generated by a simple program running on an Atmel AVR AT32UC30512C microcontroller that utilized a built-in 3-channel timer/counter to toggle digital pins' between high (3.3 V) and low (0 V) states. First, two channels generated square waves with slightly different frequencies f and $f + \Delta f$ that were converted to LED current to modulate excitation light and thus fluorescence intensity. On the third channel, a square wave with frequency f was generated and served as a reference signal for lock-in detection of the fluorescence envelope.

The beat signal coming from the photodiode was collected via a National Instruments USB-6251 digital-to-analog converter input. A LabVIEW program was used to perform digital envelope filtering of the signal and generate corresponding analog signal on USB-6251 digital-to-analog output. The phase difference θ between the filtered signal and the generated reference signal was measured with a Stanford Research Systems' SR850 DSP Lock-in amplifier. Another LabVIEW program was used to access the amplifier through a GPIB interface for data recording. A simplified signal map of the setup can be seen in Fig. 4.

C. Experimental setup

The developed optical differential temperature sensor was tested with the following experimental setup. One of the fibers with an $\text{Sm}^{2+}:\text{SrFCl}$ crystal at the end was placed into a thermostat with relatively large heat capacity and temperature equal to the ambient temperature ($T_2 = T = 23.2^\circ\text{C}$). The second fiber was placed into a thermostat with smaller heat capacity located on a heater coupled with a magnet mixer. Both thermostats were filled with water as a heat capacitor media. The heater was used to gradually raise the smaller thermostat temperature T_1 . The mixer increases the rate of heat convection and thereby rapidly achieves a state of thermal equilibrium. Alongside the optical temperature sensors were placed temperature probes of the Automatic Systems Laboratories Precision Thermometer F150. In differential mode, this enables obtaining reference temperature difference between two thermostats with a precision of $\Delta T = 0.001^\circ\text{C}$. Finally, a LabVIEW program was used to record and visualize the collected data. The scheme of the setup can be seen in Fig. 5.

D. Experiment

The first experiment started with both thermostats at a temperature close to the ambient room temperature $T_1 = T_2 = T = 23.2^\circ\text{C}$. The optical sensor's main excitation modulation frequency $f = \omega/2\pi = 1/2\pi \tau \approx 3\text{ kHz}$ was chosen and Δf was set to 2.25 Hz – the minimal achievable value due to the digital nature of the AVR microcontroller. Next was recorded, corresponding to $T = 0^\circ\text{C}$, the initial phase shift θ_0 between the generated reference signal and the fluorescence envelope signal. This was nonzero as a result of delay caused by electronic components and digital envelope filtering. As a constant for all measurements, θ_0 was subtracted from further measurements so that $\theta_{T=0} = 0^\circ$ and $\theta_{T \neq 0} = \theta$ is caused purely by temperature difference between the two probes.

Temperature differences $\Delta T = T_1 - T_2 = 0^\circ\text{C}$ were created by turning on the heater and increasing the temperature of one of the probes $T_1 \rightarrow T'_1 > T_2$. We used the heater's

controller to maintain small step sizes $\delta T_1 = T'_1 - T_1$ as constant as possible. The ASL precision thermometer provided the exact value of $\Delta T = T'_1 - T_2$ corresponding to the measured phase shift θ . This procedure was repeated multiple times to provide the dependence of phase shift on temperature difference $\theta(T)$.

Similar experiments were conducted for $f = 4.49$ and 6.73 Hz to test presented method's dependence on larger modulation frequency differences.

Duration of single point measurement was limited by the frequency difference $f = 2.25$ Hz as we require at least 0.44 seconds to measure one period of beat signal and filter the envelope. In the the experiment, we measured 2 periods of the envelope signal to obtain the phase shift during 1 second. Correspondingly, lock-in amplifier time constant of 1 s and 24 dB/oct filter with the equivalent noise bandwidth of 0.078 Hz were used. That resulted in achievement of the ultimate phase accuracy [27] determined by the limits of the analog-digital converter and further increase of time constant would not improve it.

4. Results

Fig. 6 shows the outcome of the conducted experiments. All measurements resulted in a linear dependence of phase shift θ on the temperature difference T . Changing the difference f between excitation modulation waveforms did not have a significant effect on this observed dependence. Moreover, application of linear regression to the obtained data agreed with the theoretical predictions: the slope of linear regression $\theta(T)$ is equal to $-0.97^\circ/\text{C}$ ($R^2 = 0.9988$). This slope represents the method's sensitivity $S = d(\theta)/d(T)$. Using the known parameters, the theoretical sensitivity calculated from eq. (13) and (14) results in $S = -0.96^\circ/\text{C}$ at 23.2°C and $S = -0.97^\circ/\text{C}$ at 27.2°C , which coincides well with the experimental result within the error limits.

Note that the sensitivity is not expressed in relative $\%/^\circ\text{C}$ because there is no basis to determine an absolute envelope phase in our approach and we arbitrarily define the phase shift as 0 for 0 temperature difference. This precludes the possibility of calculating a sensitivity in relative $\%/^\circ\text{C}$ and makes the concept of relative sensitivity not applicable in a straightforward manner to our novel technique.

5. Discussion

Our experiment verified that the phase shift in a beat frequency optical phase fluorimeter implemented with a rare-earth-doped crystal is able to reliably and precisely measure differential temperature with excellent sensitivity. While independently calibrated sources and phase fluoremetric detectors would actually achieve the same sensitivity, the uncertainty is significantly better with the beat frequency method as outlined below.

Consider implementation of a zero crossing technique, in a microprocessor integrated with the frequency generation unit. In this case, the time t is measured between the same phases of the fluorescence signal and excitation reference and the phase is calculated by multiplying t with the frequency. Assume that the reference starts and signal stops a counter of the

microprocessor, which counts its clock pulses. In addition, let's assume that the clock frequency is well stabilized and the phase uncertainty comes solely from the uncertainty of time measurement. The unavoidable "digital" uncertainty of time measurement δt is ± 1 clock pulse. If one uses 2 detectors to detect the sensor signals at a frequency $\omega_1 = \omega_2 = \omega$ and, respectively, 2 counters, the phase difference can be calculated as

$$\theta_2 - \theta_1 = \omega(\Delta t_2 - \Delta t_1) \quad (18)$$

and its uncertainty as

$$\delta(\theta_2 - \theta_1) = \sqrt{2} \cdot \delta t \cdot \omega \quad (19)$$

When one detects the beat signal at the frequency $\omega_1 \approx \omega_2 = \omega$, the phase difference can be calculated as

$$\Delta\theta = \Delta\omega \cdot \Delta t \quad (20)$$

and its uncertainty as

$$\delta\theta = \delta t \cdot \Delta\omega \quad (21)$$

By comparing equations (19) and (21), one observes that the accuracy is improved not only by a factor of $\sqrt{2}$ (which arises because of two separate measurements) but also by a factor $\omega / \Delta\omega$ (which is equal to about 1000 in our experiment). Accuracy is significantly improved also because the smaller (beat) frequency leads to a longer time to be measured. Another option is to raise the clock frequency of the processor, but this may be technically challenging and is certainly energy costly.

Additionally, according to the specification, the absolute phase accuracy of SR850 is $< 1^\circ$, while the relative accuracy is $< 0.001^\circ$. At least 100-fold difference in these values is common for lock-in amplifiers. Consequently, when using 2 different detectors and off-the-shelf lock-in amplifiers for measuring temperature differences, one could specify the accuracy of $< \sqrt{2}^\circ$ only. Of course, the systematic off-sets of two amplifiers can be pre-calibrated, which could improve the accuracy, at least for short-term measurements. The single detector measurements are, in general, more accurate.

It is also important to note that our theoretical section only covered the case of single sinusoidal excitation. However, our experimental results show that in practice, the technique works well for waveforms with higher frequency components, such as square waves. The actual waveform resulting from square waves is illustrated in Figure 7.

While we elected to use an orthogonal optical setup for the two excitation branches, this is by no means a requirement for implementation and therefore the proposed approach could be used to develop more convenient differential temperature sensors for a variety of applications. However, in practical implementation, it should be considered that it may not always be easy to generate waveforms with very small f using digital microcontrollers. A

high frequency on-board oscillator $f = 16\text{ MHz}$ is required for this purpose, which would raise the production cost of these differential temperature sensors. Microcontrollers, however, are usually less expensive than precise analogue systems and they also permit implementation of more complex signal processing. This would enable integration of differential temperature measurement into multiparameter tasks. For example, microcontrollers are used to control and maintain heat exchanger optimal performance, while monitoring temperature difference between heater and coolant [28].

The proposed method could be used for precise differential measurement of any parameter that affects fluorescent lifetime in a known manner, for instance local chemistry around the probe environment. The fluorescence lifetime of rare-earth-doped crystals also depends on pressure [23, 29]. In the case of $\text{Sm}^{2+}:\text{SrFCl}$ the presented method can be applied for differential pressure measurement in high-pressure equipment where changes in the range of kbar are expected and temperature is constant.

The application selected for the method will dictate the choice of thermographic phosphor. Wise material selection could increase sensitivity, alter the applicable temperature ranges, or give a stronger fluorescence signal and hence better signal-to-noise ratio. The size of sensing media can also be adjusted according to the application. There is a high demand in nano- and biotechnology for accurate noncontact temperature measurements down to the nanoscale. For example, to detect cancer in a single living cell by measuring its temperature (or other parameters affecting fluorescence as mentioned above) or to improve stability in nanolithography [30]. Therefore, with the choice of appropriate materials like rare-earth-doped crystals, quantum dots or biomorphic phosphors, our method can become a powerful tool for tackling science frontiers.

6. Conclusion

We have demonstrated a new method for differential temperature measurement based on beat signal phase fluorometry of thermographic phosphor probes. This is achieved by modulating the excitation light intensity at slightly different frequencies. A corresponding optical differential temperature prototype was developed and used in experiments that verified the high sensitivity $S = -0.97^\circ\text{C}$ (at T_0 around 23.2 to 27.2 °C) theoretically predicted for a $\text{Sm}^{2+}:\text{SrFCl}$ rear-earth-doped crystal. Advantages, possible applications and practical limitations were discussed.

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REFERENCES

1. Allison SW, Gillies GT, "Remote thermometry with thermographic phosphors: Instrumentation and applications" *Review of Scientific Instruments*, 68 (7), 2615–2650 (1997)
2. Brübach Jan, Pflitsch Christian, Dreizler Andreas, Atakan Burak, "On surface temperature measurements with thermographic phosphors: A review" *Progress in Energy and Combustion Science*, 39 (1), 37–60 (2013)
3. Abram Christopher, Fond Benoît, Beyrau Frank, "Temperature measurement techniques for gas and liquid flows using thermographic phosphor tracer particles", *Progress in Energy and Combustion Science*, 64, 93–156 (2018)
4. Chen D, Wan Z, and Liu S, "Highly Sensitive Dual-Phase Nanoglass Ceramics Self-Calibrated Optical Thermometer," *Analytical Chemistry* 88 (7), 4099–4106 (2016) [PubMed: 26937775]
5. Kolesnikov IE, Kalinichev AA, Kurochkin MA, Golyeva3 EV, Kolesnikov E. Yu., Kurochkin AV, Lähderanta E and Mikhailov MD, "YVO₄:Nd³⁺ Nanophosphors as NIR-to-NIR Thermal Sensors in Wide Temperature Range," *Scientific Reports* 7, 18002 (2017) [PubMed: 29269787]
6. Rai VK, "Temperature sensors and optical sensors," *Appl. Phys. B*, 88(2), 297–303 (2007)
7. Wang X, Liu Q, Bu Y, Liu C, Liu T and Yan X, "Optical temperature sensing of rare-earth ion doped phosphors," *RSC Adv*, 5(105), 86219 (2015)
8. Zhou Y, Qin F, Zheng Y, Zhang Z, and Cao W, "Fluorescence intensity ratio method for temperature sensing," *Opt. Lett* 40(19), 4544–4547 (2015) [PubMed: 26421577]
9. Gao G, Busko D, Kauffmann-Weiss S, Turshatov A, Howard IA, and Richards BS, "Wide-range non-contact fluorescence intensity ratio thermometer based on Yb³⁺/Nd³⁺ co-doped La₂O₃ microcrystals operating from 290 to 1230 K," *J. Mater. Chem. C*, 6(15), 4163 (2018)
10. Kommididi PR, Rami Reddy B, "Fluorescence lifetime sensing of temperature," *Proc. SPIE* 6377 (2006)
11. Katsumata T, Mochida S, Kubo H, Usui Y, Aizawa H, Komuro S, Morikawa T, "Fluorescence thermometer based on phase angle measurement," *Proc. SPIE* 5855 (2005)
12. Steinegger A, Klimant I and Borisov SM, "Purely Organic Dyes with Thermally Activated Delayed Fluorescence—A Versatile Class of Indicators for Optical Temperature Sensing," *Advanced Optical Materials*, 5(18) 1700372 (2017)
13. Bur AJ, Vangel MG and Roth SC, "Fluorescence based temperature measurements and applications to real-time polymer processing," *Polymer Engineering and Science*, 41(8), 1380–1389 (2001)
14. Yan D, Lu J, Ma J, Wei M, Evans DG and Duan X "Reversibly thermochromic, fluorescent ultrathin films with a supramolecular architecture," *Angew. Chemie*, 50(3), 746–749 (2011)
15. Maestro LM, Jacinto C, Silva UR, Vetrone F, Capobianco JA, Jaque D and Sole JG, "CdTe quantum dots as nanothermometers: towards highly sensitive thermal imaging," *Small*, 7(13), 1774–1778 (2011) [PubMed: 21567943]
16. Pandey A and Rai VK, "Rare Earth Doped Materials for Temperature Sensors," in *Spectroscopic Techniques for Security Forensic and Environmental Applications of Dwivedi Y, Rai SB and Singh JP* (Nova science publisher, 2014)
17. Farah JS, Silva MC, Cruz AG and Calado V, "Differential calorimetry scanning: current background and application in authenticity of dairy products," *Current Opinion in Food Science*, 22, 88–94 (2018).
18. Ko MJ, "Analysis and Optimization Design of a Solar Water Heating System Based on Life Cycle Cost Using a Genetic Algorithm," *Energies*, 8, 11380–11403 (2015)
19. Cuadras Àngel and Casas Óscar, "Determination of Heart Rate Using a High-Resolution Temperature Measurement," *IEEE Sensors Journal*, 6(3) (2006)
20. Von Hollen Dirk, "Differential temperature sensor device for use in the detection of breast cancer and breast disease," *United States Patent* 6086247 (2000)
21. Tong L, Li X, Zhang J, Xu S, Sun J, Zheng H, Zhang Y, Zhang X, Hua R, Xia H, and Chen B, "NaYF₄:Sm³⁺/Yb³⁺@NaYF₄:Er³⁺/Yb³⁺ core-shell structured nanocalorifier with optical temperature probe," *Opt. Express* 25, issue 14, 16047–16058 (2017) [PubMed: 28789113]

22. Xiang S, Chen B, Zhang J, Li X, Sun J, Zheng H, Wu Z, Zhong H, Yu H, and Xia H, "Microwave-assisted hydrothermal synthesis and laser-induced optical heating effect of NaY(WO₄)₂:Tm³⁺/Yb³⁺ microstructures," *Opt. Mater. Express* 4, 1966–1980 (2014)
23. Jaanisoo Raivo and Bill Hans, "f-f and f-d transition interference in Sm²⁺:SrFCl," *Physical Review. B, Condensed Matter*, 44(5), 2389–2392 (1991)
24. Shen YR and Bray KL, "Effect of pressure and temperature on 4f-4f luminescence properties of Sm²⁺ ions in MFCl crystals (M=Ba, Sr, and Ca)," *Physical Review B*, 58(18), 11944–11958 (1998)
25. Lakowicz JR, *Principles of Fluorescence Spectroscopy* (Springer, 2006)
26. Spencer RD and Weber G, "Measurements of subnanosecond fluorescence lifetime with a cross-correlation phase fluorometer," *Ann. NY Acad. Sci*, 158, 361–376 (1969)
27. Walker WD, "Sub-microdegree Phase Measurement Technique using Lock-in Amplifiers", *IEEE International Frequency Control Symposium*, 825–828 (2008)
28. Honeywell Process Solutions, "SmartLine Differential Temperature Measurement for Improved Heat Exchange Performance" (2016)
29. Jovani B et al., "Pressure Effects on the Optical Properties of LuVO₄:Eu³⁺ Nanoparticles," *International Letters of Chemistry, Physics and Astronomy*, 75, 1–10 (2017)
30. Lee J and Kotov NA, "Thermometer design at the nanoscale," *Nano Today*, 2(1), 48–51 (2007)

Fig. 1.
Beat signal from fluorescence of two fluorophores excited at slightly different optical frequencies and corresponding detected envelope.

Fig. 2. Sm²⁺:SrFCl absorption (violet) and emission (red) spectra alongside with the emission spectrum of the excitation LED (blue line) and transmission of the interference filter (dark red) used in the experimental temperature sensor. The inset shows the temperature dependence of lifetime at the fluorescence maximum corresponding to the $^5D_1 \rightarrow ^7F_0$ transition (which is the origin of the arrow pointing to the inset). Plot based on data from [24].

Fig. 3. Schematic of the optical temperature sensor that shows mutual position of the LEDs, excitation filters (1), dichroic mirrors (2), quartz spherical lens (3), optical fibers (4), $\text{Sm}^{2+}:\text{SrFCl}$ crystals (5), fluorescence interference filters (6) and photodiode within anodized aluminum frame.

Fig. 4.
Simplified signal map of conducted experiment.

Fig. 5.

Drawing of experimental setup. Number 1 denotes the thermostat with smaller heat capacity and temperature T_1 . Number 2 corresponds to the thermostat with the bigger heat capacity and temperature T_2 , maintained at ambient room temperature $T = 23.2\text{ }^{\circ}\text{C}$.

Fig. 6.
Measured $\Delta\phi(T)$ in the case of $f = 2.25$ (blue), 4.49 (green) and 6.73 (red) Hz. R^2 of linear fit = 0.9988.

Fig. 7.
Simulated luminescence beat signal in case of excitation by square waves with $\omega/\omega = 0.05$