A novel optical thermometry strategy based on upconversion emission of Tm^{3+}/Yb^{3+} codoped $Na_3GdV_2O_8$ phosphors.

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Abstract

In the last few years, huge progress has been devoted to the development of remote optical thermometry, due to their non-contact, high-sensitivity and fast measurement characteristics, which is especially important for various industrial and bio-applications. For these purposes, lanthanide-doped particles seem to be the most promising luminescence thermometers. In this study, $Na_3GdV_2O_8$ (NGVO): Tm^{3+}/Yb^{3+} phosphors are prepared by sol gel method. Under 980 nm excitation, the upconversion emission spectra are composed of two visible emission bands arising from the Tm^{3+} transitions $^1G_4 \rightarrow {}^3H_6$ (475 nm), $^1G_4 \rightarrow {}^3F_4$ (651 nm), a strong emission at 800 nm ($^3H_4 \rightarrow {}^3H_6$) in the first biological window and an emission in the third biological window at 1625 nm ($3F_4 \rightarrow {}^3H_6$). Accordingly, the luminescence intensity ratio (LIR) between the Tm^{3+} $LIR_1(^3H_4/^1G_4)$ and LIR_2 ($^3F_4/1G_4$)) transitions demonstrates excellent relative sensing sensitivity values (4.2 % K^{-1} – 2% K^{-1}) and low-temperature uncertainties (0.4 K–0.5 K) over a wide temperature sensing range of 300 K to 565 K, which are remarkably better than those of many other luminescence thermometers. The NGVO: Tm^{3+}, Yb^{3+} exhibit a stronger NIR emission at low excitation density that has potential uses in deep tissue imaging, optical signal amplification and other fields. The results indicate Tm^{3+}/Yb^{3+}: NGVO is an ideal candidate for optical thermometer and particular for biological applications.

Keywords: Biological applications, luminescence thermometry, optical sensors, luminescent nanomaterials, non-thermally coupled levels, lanthanide ions.

1. Introduction

Real-time temperature detection plays an important role in industry, manufacturing, formation of metal alloys, climatology, scientific research, biological and medical applications.[1–7] Luminescent thermometers, such as lanthanide-based, dye-based, QD-based, and polymers-based probes, have been widely investigated among reported types of thermometers (thermocouple, thermistors, thermal cameras, and so on) because of their noninvasiveness, short acquisition time, high spatial resolution, and high sensitivity.[8–12] Temperature-dependent fluorescence bandwidth, lifetime, band shape, spectral shift, or polarization can all be used to create these luminous thermometers.[13–15].Temperature assessment in complex settings with lanthanide-based luminescence intensity ratio (LIR) thermometry is promising, since it is free of issues caused by changes in probe concentrations and variations in light excitation and detection efficiency. Lanthanide-based LIR thermometry typically employs two thermally coupled energy levels in one lanthanide ion, two non-thermally coupled energy levels in one lanthanide ion, or temperature dependent energy transfer processes between two lanthanide ions, with the empirical exponential or linear growth equation for temperature evaluation.[9,16] In order to deeper tissue penetration, it will be crucial to design a luminescent thermometer, including the first biological (NIR-I: 650-950 nm), the Second (NIR-II: 1000−1350 nm), and the Third (NIR-III: 1500–1850 nm) for excitement and the detection of the biological optical transparency windows.[17–19] According to reports on the luminescence behaviors of rare earth elements, upon 975 nm excitation, Tm^{3+} ions can emit in visible at 475 nm, NIR-I at 800 nm and NIR-III at 1625 nm emissions, which are located within NIR-I and NIR-III, respectively, and they are attributed to the $^3H_4$ to $^3H_6$ and $^3F_4$ to $^3H_6$ radiation transitions respectively. [20,21] Meanwhile, Yb^{3+} ions emit the luminous band at NIR-II, which corresponds to the $^2F_{5/2}$-$^2F_{7/2}$ transition, and they can also function as a sensitizer to enhance Tm^{3+} emission.[22] Based on these findings, a thermometer doped with both Tm^{3+} and Yb^{3+} may be able to achieve simultaneous emission bands in NIR-I and NIR-III using a 975 nm excitation. Moreover, the host material has a significant impact on luminous and sensing characteristics. Without a doubt, the Vanadate group $(VO_4)^{3-}$, in which the core metal ion V^{5+} is coordinated by four oxygen ions to create a tetrahedral with T_d symmetry, is a highly efficient luminous center [23]. Double vanadate phosphors with significant UV and near-UV absorption and a wide luminescence area have been recommended as potential RE^{3+} ion hosts. To our knowledge, this is the first use of emissions ranging from visible to NIR III from a single combination of dopant / sensitizer ions $(Tm^{3+}$ / $Yb^{3+})$ in the detection of temperature. In this study, NGVO: Tm^{3+}/Yb^{3+} phosphors are prepared by sol gel method. The upconversion emission spectra of the Yb^{3+}/Tm^{3+} codoped NGVO phosphors have been investigated under 975 nm excitation.

The upconversion mechanism processes are analyzed. The optical temperature sensing characteristics based on non-TCLs are discussed by using the LIR technique.

2. Experimental

2.1 Synthesis of Yb^{3+}/Tm^{3+}: $Na_3Gd (VO_4)_2$ phosphors

A simple citrate-based sol-gel method was used to make NGVO Tm^{3+}/Yb^{3+} phosphors. Sigma-Aldrich Co. provided the raw ingredients, which included $NaNO_3$, $Tm (NO_3)_2*5H_2O$, NH_4VO_3, $Yb (NO_3)_3*5H_2O$, $Gd (NO_3)3*5H2O$, and citric acid. The proper amount of all constituents was weighted and dissolved into 75 ml of de-ionized water to produce a homogeneous mixture based on the stoichiometric ratio. The citric acid was then added to the aforementioned solution. The citric acid was then added to the aforementioned solution. Citric acid has a molar concentration ratio of 2:1 to total metal ions. The solution was then sealed with a polyethylene lid and heated for 30 minutes at 80°C with vigorous mechanical stirring. The lid was removed from the beaker once the solution's color was altered from yellow to blue, and the solution was allowed to evaporate, resulting in the gray wet-gel. The xerogel was then obtained following a 12-hour heat treatment in a 120°C oven. Finally, the xerogel was placed in an alumina crucible and calcined for 5 hours at 600 °C.

2.2 Characterization

The X-ray diffraction (XRD) measurements were performed with a Bruker AXS D8 Advance diffractometer. The XRD data were collected in a scanning mode with a step size of 0.015° from 20° to 70°. Diffuse reflectance spectrum was taken out by the use of a Lambda 365 UV-vis spectrometer (PerkinElmer) in the 220-1100 nm range.

The upconversion emission spectra were acquired with an Andor Shamrock 500 spectrometer connected to the silicon or InGaAs CCD cameras, and the apparatus response was adjusted. As an excitation source, a tunable continuous wave (CW) Ti: sapphire laser system (Spectra Physics 3900-S, pumped by a 15 W 532 nm Spectra Physics Millenia) was tuned to 975 nm (10 mW; spot size 0.2 mm). The luminescence decay curves were monitored using an analogic storage oscilloscope (LeCroy WS424) connected to the detection system and a pulsed parametric oscillator OPO (EKSPLA/NT342/3/UVE) laser to excite the sample.

3. Results and discussion

3.1 Structure and morphology

Fig. 1a shows the XRD patterns of the NGVO codoped Tm^{3+}/Yb^{3+}. Comparing with the standard data of NGVO (JCPDS card #49-1789), all the diffraction peaks can be indexed, and no other impurity peaks can be detected, which proves the well incorporation of Tm^{3+} and

Yb^{3+} ions in the Gd^{3+} site. The Rietveld refinement of NGVO:Tm^{3+}/Yb^{3+} phosphors was presented in **Fig. S1.** The red solid lines and the black circles represented the calculated and experimental patterns, respectively. The refined structural parameters for this phosphor were listed in **Table S1.** This indicates that the compounds under consideration had a pure monoclinic phase, and the Tm^{3+} and Yb^{3+} ions were incorporated into the host lattices without modifying the phase structure. The surface morphology and grain size distribution were examined using a scanning electron microscope (SEM). The synthesized sample had a morphology of agglomerated spheroids-shaped grains with a diameter of 0.5-1 μm on average **(see Fig. 1b)**. The observed agglomeration of grains may be due to the high annealing temperature and was also present in the NGVO :Er^{3+}.Ho^{3+}/Yb^{3+} phosphor.[26]

3.2. ~~UV VIS NIR~~ Absorption spectroscopy

Fig. 2 depicts the UV-Vis diffuse reflectance spectra of the NGVO Tm^{3+}/Yb^{3+} phosphor. It is demonstrated that these compounds displayed significant UV absorption due to the charge transfer transition of $O^{2-} \rightarrow V^{5+}$ in the VO_4^{3-} group[27]. The $^2F_{7/2} \rightarrow {}^2F_{5/2}$ (Yb^{3+}) absorption transition produces a broad absorption band with a peak at 975 nm.[28] The absorption peaks located at 682 nm and 796 nm are assigned to the transitions of $^3H_6$ to $^3F_2$ and $^3H_4$ of Tm^{3+} ions, respectively.[29]

3.3 Upconversion properties

The citrate-based sol-gel method was used to synthesize NGVO structures doped with the following concentration of doping ions: Yb^{3+} 10%/Tm^{3+} 1% [26,29]. Based on our experience and general knowledge, specified amounts of dopant ions were used in order to prevent UC luminescence quenching. ~15% of sensitizer (Yb^{3+}) and low concentrations of emitters (up to ~5%) are mostly used for UC systems, as suitable for intense emission.

After 975 nm laser excitation, the synthesized nanomaterial displays a strong, visible to the naked eye blue upconversion (anti-Stokes) luminescence. **Fig. 3** shows the upconversion emission spectra of NGVO: Tm^{3+}/Yb^{3+} crystals at room temperature. The upconversion emission spectra are composed of two visible emission bands arising from the Tm^{3+} transitions $^1G_4 \rightarrow {}^3H_6$ (475 nm), $^1G_4 \rightarrow {}^3F_4$ (651 nm), the strong emission at 800 nm attributed to the $^3H_4 \rightarrow {}^3H_6$ transition in the first biological window and an emission in the third biological window at 1625 nm, attributed to the transition $^3F_4 \rightarrow {}^3H_6$ [30], so they are especially appealing from the biological point of view. The NGVO: Tm^{3+}, Yb^{3+} exhibit a stronger NIR emission at low excitation density that has potential uses in deep tissue imaging, optical signal amplification and other fields [19,31].

The upconversion luminescence spectra of all the reported materials were analyzed using the standard Dieke's diagram of trivalent lanthanide energy levels.[32] **Fig. 4a** shows an energy level diagram for the Yb^{3+} and Tm^{3+} ions, as well as a schematic representation of the possible mechanisms responsible for the generation of upconversion luminescence. Furthermore, the intensity of anti-stokes luminescence is proportional to the excitation pump power, which is critical for understanding the upconversion mechanism. According to the theory, the integral intensity I of the upconversion emission bands depends on the excitation power P as [33,34]:

$$I=P^n \text{ (Eq 1)}$$

where n is the number of absorbed infrared photons required for the emission of one visible or infrared photon in the range of unsaturated upconversion luminescence. The dependences of the logarithm of the integral intensity I of the emission bands on the logarithm of the excitation power P of the laser excitation were determined to identify the mechanism of photon activation during the upconversion process. The number of photons (n) involved in the upconversion processes determines the slope of the associated linear fit. The integrated intensities of the anti-stokes luminescence bands for the blue and NIR of NGVO: Yb^{3+}/Tm^{3+} as a function of pump intensity on a logarithmic scale are shown **in Fig. 4b.** In the materials examined two or three-photon processes occur for blue and NIR anti-stokes luminescence. The fitted slope is 2.4 and 1.6 for the blue and NIR emission bands, respectively. This suggests that a three-photon process is designed to establish the blue, but the NIR upconversion emission at 800 nm should be the product of a two-photon process. A three-photon process involving excited Yb^{3+} ions and intermediate amounts of Tm^{3+} ions can populate the $^1G_4$ state of Tm^{3+} ions. The excited Yb^{3+} ions, in particular, can transfer their energy to the Tm^{3+} ions and excite them from the ground $^3H_6$ level to the excited $^3H_5$ level. The Tm^{3+} ions then relax non-radiatively and populate the $^3F_4$ level. The next exciting Yb^{3+} ions can use their energy to pump Tm^{3+} ions to the $^3F_4$ level, allowing the $^3F_{2,3}$ levels to populate. The Tm^{3+} ions in the $^3F_{2,3}$ levels relax non-radiatively to the $^3H_4$ level once more. The Yb^{3+} ions subsequently transfer their energy to pump the Tm^{3+} ions to the $^3H_4$ level, where they will populate the $^1G_4$ level. Finally, the excited Tm^{3+} ions in the $^1G_4$ level relax to the ground state $^3H_6$, emitting blue light at about 475 nm, while a small number of the excited ions relax to the $^3F_4$ level, emitting red light at about 651 nm. The emission of Tm^{3+} ions through their $^3H_4\rightarrow^3H_6$ transitions causes the NIR emission at 800 nm. When the energy of two excited Yb^{3+} ions (the excited Yb^{3+}–Yb^{3+} pair) is transferred to the excited levels of closely nearby $^3F_{2,3}$ and then to the $^3H_4$ level of the Tm^{3+} ions following non-radiative

relaxation, a two-photon event occurs [35–37]. The temporal evolution of the upconversion emissions under 975 nm excitation have non-exponential character. The kinetics for the 475 nm emission is represented in **Fig 4c**. As can be seen it shows a rise and a decay time that it is characteristic of the energy transfer processes.[38]

Fig. 4c shows the PL decays of the Tm^{3+} transition: $^1G_4 \rightarrow {}^3H_6$ (475 nm). The $^1G_4$ emission displays a non-exponential decay. The deviation from single exponential decay in the Tm^{3+} is ascribed to the cross relaxation between Tm^{3+} ions, which even occurs at very low concentration (1% Tm^{3+}) [35] . This result can also be explained by the introduction of extra decay pathway due to the Yb^{3+} -Tm^{3+} energy transfer leading to enhance the decay rate of $^1G_4$. The effective decay time τ_{eff} is calculated by:

$$\tau_{eff} = \frac{1}{I_0} \int_0^\infty I(t)\, dt \quad \text{(Eq 2)}$$

where I(t) denote the PL intensity as a function of time t, and I_0 represents the initial PL intensity at t = 0. From the decay curves, the effective PL lifetime τ_{eff} is calculated to 0.323 ms. From the PL decays of $^1G_4$ of Tm^{3+} in NGVO: Tm^{3+}/ Yb^{3+} (**Fig. 4c**), a build-up is clearly seen in the beginning of the curves, which is caused by feeding the $^1G_4$ state of Tm^{3+} through ET from Yb^{3+}. The rise time is calculated to be $\tau_{rise} = 0.13$ ms.

3.4 Optical temperature sensing

We altered the sample temperature to test the feasibility of employing this system for temperature sensing. **Fig. 5** show the upconversion spectra of the NGVO: Tm^{3+}/Yb^{3+} sample obtained at temperatures ranging from 300 to 565 K using a 975 nm laser.

For the $^1G_4 \rightarrow {}^3F_4$ (475 nm) $^1G_4 \rightarrow {}^3F_4$ (651 nm) transitions of the NGVO Tm^{3+}/Yb^{3+} sample, both emission intensities increase slightly before dropping drastically, which is due to an increase in non-radiative relaxation pathways of the high energy excited state, which leads to thermal quenching gradually becoming dominant as the temperature rises. Because of the thermal enhancement based on phonon-assisted energy transfer between Yb^{3+} and Tm^{3+} ions, the $^3H_4 \rightarrow {}^3H_6$ transition (800 nm) overcome typical thermal quenching and increase slightly as the temperature rises [39,40]. As a result, the inverse intensity variations between emission band pairings suggest that a double ratiometric method may be used to provide an all-optical temperature sensor. The LIR of the two specific band pair (ratio of the integrated peak areas), LIR_1 (800/475) and LIR_2 (1625/475), are therefore calculated in function of the temperature. In the temperature range of 300-565 K, **Fig. 6a-b** shows the LIR_{1-2} values as a function of temperature. The LIR values increase with temperature, and the maxima value are obtained

when the temperature reaches 565 K. The LIR_2 (1625/475) rises by almost 6 K-fold the temperature range studied whereas almost 35 K-fold enhancement was noted in the case of the LIR_1. Theoretically, the energy level gap between the couple ($^1G_4$, $^3H_4$) and ($^1G_4$, $^3H_5$) of Tm^{3+} ion are 8550 cm^{-1} and 14900 cm^{-1}, respectively.[35,41] These values are higher than 2000 cm^{-1}. Therefore, the Boltzmann equation is no longer applicable because are non-thermally coupled energy levels and the LIR can be fitted ($R^2 > 0.99$) by the following second order polynomial (**Eq. 3**), and its coefficients are given in **Table S2.**

$$LIR = \frac{A+B}{1+C*T+D*T^2} \quad \text{(Eq 3)}$$

where LIR is the ratio of the integrated emission intensities resulting from different non-TCLs; the fitting coefficients A, B, C, D, and T is the absolute temperature.

One of the most important characteristics in practical applications is the relative sensitivity (Sr), which characterizes the thermometric capabilities of the material and may be determined using the following formula:

$$Sr = \frac{1}{LIR} * \partial LIR / \partial T \quad \text{(Eq 4)}$$

where ∂LIR represents the change of LIR corresponding to the ∂T change of temperature. The S_r allows for the quantitative assessment of different levels over a wide variety of temperature ranges.

Fig.7 shows how the values of S_r change with temperature for LIR_1 and LIR_2. On the other hand, usually S_r values decrease when the temperature rises for many lanthanides and transition ions. Fortunately, by employing the band intensity ratios of Tm^{3+} (800/475) and (1625/475), it is feasible to maintain the great sensitivity of temperature sensing since S_r rises with temperature, being approximately 4.2% K^{-1} and 2.0% K^{-1} above 565 K for these non-TCLs. The Tm^{3+} activated optical temperature sensing materials and their performance investigated in recent years are given in **Table 1** for evaluation of the optical temperature sensor performance of Tm^{3+}/Yb^{3+} codoped NGVO. Moreover, in this table are included values for the relative sensitivity obtained with other lanthanide or transition elements. As can be seen, the values obtained for LIR_1 shows the highest values for the relative sensitivity. The temperature resolution (δT) associated with both band intensity ratios were estimated and utilized to further investigate the efficiency of the suggested high -temperature sensor. This resolution temperature can be obtained from:[42]

$$\delta T = \frac{1}{S_R} \frac{\partial LIR}{LIR} \quad \text{(Eq 5)} \quad \text{(Eq 4)}$$

where δLIR is the thermometric parameter's resolution limit or relative uncertainty, that is, the smallest change in ratio that can be observed experimentally. The resolution limit is connected to thermometer performance, but it is also affected by the experimental setup [3,34]. As a result, utilizing improved acquisition methods as well as improving measurement performance, such as extending integration time and using the average of successive measurements to reduce experimental noise, might be one option to enhance the resolution limit. To determine the limit of detection, 100 measurements were performed at room temperature under similar conditions for Tm^{3+}/Yb^{3+} co-doped NGVO and the results are presented in the histograms shown in **Fig. 8a-b**. LIR uncertainty (δLIR) was obtained as the statistical distribution's standard deviation for each method with values of 0.66 and 0.87 for the LIR_1 and LIR_2, respectively. Using the Eq. 5, the values are lower than 0.5 K indicating that both LIR techniques have a high precision in all this temperature range.

It is worth noting that in the vast majority of reports, only the maximum S_r and minimum T values are compared to other literature data (**Table 1**). However, because of the various temperature measurement ranges and the character dependent on S_r and T temperatures, such comparisons are not entirely useful. As a result, while evaluating the performance of different optical thermometers, the best, most often used operating temperature value should be chosen. In our case, the band ratios LIR_1 (spectral range suitable for electronics and other industrial applications) have an excellent $S_r= 4.2$ % K^{-1}, while the LIR_2 band ratio (located in biological spectral range) has an excellent $S_r=2.0$ % K^{-1}, with good thermal resolutions of 0.4 K at 300 K. The results indicate Tm^{3+}/Yb^{3+}: $Na_3GdV_2O_8$ is an ideal candidate for optical thermometer.

Table 1. Maximum Relative Temperature Sensitivities Sr at 300 K and at the highest measured temperature (T_{max}) for different luminescent materials.

Materials	T-range (F	S_r (% K⁻ at 300F	S_r (% K⁻ at T_{max}	δ1 (K	Ref
YVO_4: Eu^{3+}	123-573K	1.38	-	0.5	[43]
$La_2Mo_3O_{12}$: Pr^{3+}	298-598	0.9	1.94	-	[44]
$K_7ZnSc_2B_{15}O_{30}$: Mn^{2+}	300-525	0.01	1.84	0.8	[45]
$Bi_2Al_4O_9$: Cr^{3+}	100-600	1.24	0.4	0.2	[46]
Gd_2ZnTiO_6: Er^{3+}/Yb^{3+}	313-473	3.98	0.60	-	[47]
$Ba_3Y_4O_9$:Er^{3+}/Yb^{3+}	298-573	1.31	0.36	-	[48]
$NaLaMgWO_6$:Er^{3+} / Mo⁶	323-473	1.32	0.53	-	[49]
$BaLa_4Si_3O_{13}$: Dy^{3+}/Eu^{3+}	298-523	0.1	1.36	-	[50]

Material	Range (K)		S_r (% K^{-1})		Ref.
LuNbO$_4$: Pr^{3+}/Tb^{3+}	283-493	0.1	1.26	-	[51]
LaNbO$_4$:Bi^{3+}/Tb^{3+}	303–483	0.2	1.2	-	[52]
La$_2$MgGeO$_6$:Bi^{3+}/Mn^{4+}	293–473	0.28	2.5		[53]
Sr$_2$NaMg$_2$V$_3$O$_{12}$:Eu^{3+}	100-500	0.5	1.5	0.?	[54]
Ba$_3$Y$_4$O$_9$:Ho^{3+}/Tm^{3+}/Yb^3	298-573	0.25	1.2		[55]
NaBiF$_4$: Tm^{3+}/ Yb^{3+}	303-443	0.7	1.1	-	[56]
Y$_2$Ti$_2$O$_7$: Tm^{3+}/Yb^{3+}	300–400	0.4	0.87	-	[57]
GdVO$_4$:Tm^{3+}//Yb^{3+}	297−673	0.4	1.54	0.?	[58]
NaY$_2$F$_7$:Tm^{3+}/Yb^{3+}	300-567	0.5	1.2	-	[59]
Ba$_3$Y$_4$O$_9$:Tm^{3+}/Yb^{3+}	298-573	0.9	0.55	-	[60]
Na$_3$GdV$_2$O$_8$: Tm^{3+}/Yb^{3+}	300-565	0.93	4.2	0.4	This work (LIR$_1$)
Na$_3$GdV$_2$O$_8$: Tm^{3+}/Yb^{3+}	300-565	1.34	2.0	0.4	This work (LIR$_2$)

4. Conclusion

In this study, a novel optical thermometry strategy based on upconversion emission of Tm^{3+}/Yb^{3+} codoped NGVO phosphors were developed. NGVO: Tm^{3+}/Yb^{3+} nanostructure phosphors are prepared by sol gel method. As the RE ions are incorporated into the host lattice, the XRD study shows that the as-prepared sample is single phase. The upconversion emission spectra are composed of two visible emission bands arising from the Tm^{3+} transitions $^1G_4 \rightarrow {}^3H_6$ (475 nm), $^1G_4 \rightarrow {}^3F_4$ (651 nm), a strong emission at 800 nm attributed to the $^3H_4 \rightarrow {}^3H_6$ transition in the first biological window and an emission in the third biological window at 1625 nm, attributed to the transition $^3F_4 \rightarrow {}^3H_6$. This stronger NIR emission at low excitation density has potential uses in deep tissue imaging, optical signal amplification and other fields. This is the first use of emission ranging from visible to NIR III from a single combination of dopant / sensitizer ions (Tm^{3+} / Yb^{3+}) in the detection of temperature. The LIR$_1$ (800/475) presents an important S_r value of 4.2% K^{-1}. The LIR$_2$ (1625/475) has as well an excellent S_r = 2.0% K^{-1}, with good thermal resolutions of 0.4 K at 300 K. Furthermore, by employing the band intensity ratios of Tm^{3+} (800/475) and (1625/475), it is feasible to maintain the great sensitivity of temperature sensing since S_r rises with temperature, being approximately 4.2% K^{-1} and 2.0% K^{-1} above 565 K for these non-TCLs. The results indicate Tm^{3+}/Yb^{3+}: NGVO is an ideal candidate for optical thermometer.

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