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Er³⁺ doped nanoparticles as upconversion thermometer probes in confined fluids†

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Non-contact temperature measurement at the nanoscale by photoluminescence using a nano-sensor in a confined fluid has been performed in the present work. Upconversion lanthanide-doped nanoparticles applied to ratiometric thermometry could be considered as a self-referenced nanosensor. Gadolinium orthovanadate (GdVO₄) nanoparticles doped with Yb³⁺ and Er³⁺ were synthesized and then dispersed in an ester-based fluid. Rheological measurements show that the viscosity of the dispersed NP suspension remains unchanged up to a shear rate of 10⁻⁴ s⁻¹ at 393 K. The NP suspension allows luminescence intensity ratio (LIR) thermometry up to 473 K with a relative sensitivity of 1.17% K⁻¹ with a NIR laser. Then, the temperature calibration by coupling the high pressure (1.08 GPa max) confirmed the applicability of NPs as a thermosensor in a variable pressure environment. According to these results, the fluid containing GdVO₄:Yb³⁺/Er³⁺ nanoparticles can be used for temperature sensing in a pressurized environment for further application in tribology.

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1. Introduction

Temperature and pressure are fundamental parameters affecting the physicochemical properties of materials. Their measurements are crucial for both scientific and industrial applications. In many applications, they have to be measured locally in submicron-sized areas: nano-manometry and mano-thermometry in biomedical applications, microfluidics, and catalysis as well as in tribology. In tribological measurements, temperature and pressure are crucial parameters for understanding and predicting the behavior of the interface between solids in contact. Local temperature and pressure changes between two contacting friction surfaces affect the rheological properties of the interface, which has an important influence on the life and performance of the tribological system.^{1,2} To understand the friction between two materials in contact, local temperature and pressure measurement with high accuracy and efficiency has become a major topic in tribology research. Well-known techniques for measuring temperature in friction include (1) a thermocouple inserted in the material 2 mm

below the sliding surface; (2) infrared thermography; and (3) Raman micro-spectroscopy.^{3,4} However, reliable measurement with good spatial and temporal resolution of temperature, or other physical parameters in frictional contact is not a simple matter.

The application of Raman spectroscopy to tribological measurements has recently been studied for local pressure mapping in the case of lubricated contact with a fluid by Jubault *et al.*^{5,6} and Yagi *et al.*⁷ In such experiments, this technique provides a precise and accurate pressure measurement with a higher spatial and temporal resolution than other temperature measurement techniques. However, it requires the selection of a fluid that exhibits strong Raman scattering, which is not the case for most lubricants. Infrared thermography collects the IR emission from the tribological contact. It is then possible to measure the temperature all over the contact area by using a full-field IR camera. A drawback of this technique is the calibration process. Indeed, different sources (solid surfaces and bodies, lubricant films or the interface and the environment) contribute to the overall IR radiation and must be separated by applying appropriate coatings to the transparent disc and/or using different filters. These issues can be solved using non-contact nano-manometers and nanothermometers. Recent studies have been carried out by Albahrani *et al.*⁸ and Seoudi *et al.*⁹ on the application of a nano-sensor for measuring temperature and pressure in a lubricating fluid. In their studies, CdSe/CdS/ZnS core/shell/shell quantum dots (QDs) were used as a calibrated nano-sensor for temperature and pressure

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(under 0.2 to 1.3 GPa between 0 and 100 °C) by their change in emission energy shift. The main drawback of this technique was the coupled dependence of the emission energy to pressure and temperature, while pressure and temperature generally vary independently in tribological contact.

It is therefore essential to find out a suitable optical thermometric sensor for temperature measurement under multivariable conditions. In tribological measurement, pressure independence should be required. Meanwhile, to reduce the measurement scale to achieve high spatial resolution, the miniaturized size of the sensor is one of the most important conditions. Over the past decades, many photoluminescent nanothermometers have been studied, such as fluorescent dyes^{10–12} and CdSe-based^{9,13} and perovskite based^{14,15} quantum dots. Temperature sensitivity could be demonstrated by their spectroscopic properties, such as emission spectral shift, variation in emission intensity, and change in emitter lifetime. Among the spectral variables of thermometry, the luminescence intensity ratio (LIR) is well-known as a self-referenced measurement method, which will not be influenced by the absolute intensity of the emission.^{16–25} This feature is particularly needed in dynamic measurement, where the sensor concentration cannot remain constant. Nanoparticles doped with lanthanide ions (Ln³⁺)^{26,27} are one of the main families of photoluminescence nanothermometers and are commonly used as LIR thermometers. Thanks to the special property of Er³⁺, it provides thermally coupled energy levels (²H_{11/2} and ⁴S_{3/2}) that are suitable for temperature measurement in the range 293–473 K, with high sensitivity.^{28–32} The relatively small gap between the energy levels (about 600–800 cm⁻¹) allows excited electrons to be thermally promoted to a higher level. The proportion of thermally promoted electrons follows the Boltzmann distribution,³³ which allows the temperature to be calibrated by measuring the ratio of the emission intensity of its two thermally coupled energy levels. Besides the aforementioned favorable luminescence properties, they exhibit also relatively low cytotoxicity, resistance to photobleaching, thermal decomposition and oxidation processes. Therefore, they can be used in various applications including biomedical ones.

However, considering the scattered medium for the Er³⁺-based fluorescence sensor in temperature measurement, the current excitation by laser of Er³⁺ under green light can cause interfering emission from the scattered medium. To solve this problem, the Er³⁺-based fluorescence sensor could be excited *via* an upconversion (UC) system, with low-energy absorption to induce high-energy emission.^{34,35} Er³⁺ combined with a sensitizing ion such as Yb³⁺ can be excited using a near-infrared (NIR) laser *via* the energy transferred by Yb³⁺. The use of an NIR excitation source avoids the possible emission of scattered media during the visible excitation.^{36,37} In the UC system, several experimental parameters need to be carefully controlled to obtain accurate Er³⁺ thermometry, such as the effects induced by the NIR laser,^{29,38–41} the optical quenching effect^{42–45} and the chemical properties of the sensor.^{46–49} These parameters can be affected by other physical influencing factors. As an example, in tribological applications, local pressure can cause potential damage or material degradation. Under high pressure, the

nano-sensor could be modified and thus its optical properties could change.^{50,51} Studies in the literature have shown that high pressure (up to 25 GPa) can cause variations in Er³⁺-doped materials due to structural changes such as shortening of interionic distances and shifting energy levels. These variations modify the probability of transitions and therefore have an impact on the position and intensity of the photoluminescence peak.^{52–58} Since the inorganic structure is stable under compression, a relatively high pressure is usually required to cause a structural variation. Under low-range pressure (below 6 GPa), the pressure sensitivity on SrF₂:Yb³⁺,Er³⁺ has been reported in Runowski's works in 2017, variations in lifetime, emission intensity and peak centroid were observed under compression up to 5.5 GPa.⁵⁷ Moreover, the pressure-sensing properties of upconversion Yb³⁺/Er³⁺ doped fluoride nanoparticles have also been found to vary the red-to-green ratio, lifetime and brightness of Er³⁺ with pressure up to 5.4 GPa by McLellan *et al.*⁵⁸

Nonetheless, pressure sensitivity up to 1 GPa has not yet been reported by Ln-doped nanoparticles. As mentioned previously, for further application in tribology, the temperature measurement must be stable under specific conditions, such as high pressure (up to 3 GPa) and high shear rates (up to 10⁶ s⁻¹). Indeed, besides temperature, pressure and shear stress are the other two key parameters that vary in tribological contact. In this work, we studied the effect of a more moderated pressure (up to 1 GPa) on the LIR thermometry of Er³⁺-doped nanoparticles. As the nano-sensor will be used in a specific medium for further tribological measurements, the GdVO₄:Yb³⁺/Er³⁺ upconversion nano-sensor was synthesized and then dispersed in a lubricant (ester-based oil). Among the various possible matrices, it offers a number of advantages, including very simple synthesis in the form of very small particles (< 50 nm). The hydrophilic surface of the nanoparticles after co-precipitation synthesis means that the dispersion of the nanoparticles in the lubricant can be optimised for future tribological applications. Moreover, the vanadate matrix provides very good sensitivity for Er³⁺/Yb³⁺ thermometry.^{59,60} It has the disadvantage of having a fairly high phonon energy,⁶¹ but our previous study has already shown that this disadvantage is negligible in low concentration suspension.⁶² The thermometric characteristics have also been studied as a function of dispersion and laser power conditions.⁶² As GdVO₄ is known to exhibit a phase transition from a zircon-like to a scheelite-like structure at 6.8 GPa, this nanosensor should be used exclusively in a pressure range below 6 GPa.⁶³ The concentration of NPs GdVO₄:Yb³⁺/Er³⁺ in the suspension was selected according to hydrodynamic size and rheological properties. The photoluminescence thermometry of the dispersed GdVO₄:Yb³⁺/Er³⁺ nano-sensor was characterized up to 423K. The effect of pressure on the dispersed suspension of the GdVO₄:Yb³⁺/Er³⁺ nano-sensor was studied in a diamond anvil cell (DAC) at pressures up to 1 GPa and at different temperatures.

2. Materials and methods

2.1. Materials

GdVO₄:Yb³⁺/Er³⁺ (*x*(Yb) = 0.10; *x*(Er) = 0.02) Nanoparticles were synthesized by a chemical co-precipitation technique.^{16,26,64–66}



The precise synthesis method can be found in our previous work.⁶²

Suspension of NPs GdVO₄. Yb³⁺/Er³⁺ was prepared by adding the ground powder in an ester-based oil (Nycobase 5750: conventional mono-pentaerythritol lubricating oil, supplied by NYCO, Paris, France) at various weight concentrations, followed by mechanical stirring and ultrasonic treatment at room temperature for 30 minutes.

2.2. Characterizations

The crystalline phase of the synthesized nanoparticles was characterized using an X-ray diffractometer (Bruker D8 Advance diffractometer) with Cu K α radiation ($\lambda = 1.54060 \text{ \AA}$) operating at 45 kV and 30 mA at room temperature. Scanning electron microscopy (Zeiss Merlin Compact SEM) is performed for the analysis of the morphology, using a secondary electron detector at a low accelerating voltage up to 5 kV. The morphology of the nanoparticles was analyzed by transmission electron microscopy (TEM, JEOL 2100F 200 kV) with a secondary electron detector. The hydrodynamic size of the NPs in the suspension was calculated by the Dynamic Light Scattering (DLS, Malvern-Zetasizer) at different concentrations.

The viscosity of the colloidal suspension was determined using a rheometer (Physica MCR301, Anton Paar) with a parallel-plate geometry (PP40), at different temperatures (293–373 K, $\pm 0.03 \text{ K}$) and imposing a shear rate (range between 1 and 10^4 s^{-1}). During the measurement, a steel plate is rotating against a glass plate, and the gap between the two parallel plates was fixed at 0.2 mm. A transparent glass plate will be used for further optical measurement. The uncertainty on viscosity measurement is about 5%.

For the optical characterizations, the absorption spectrum of the NPs powder was acquired using a LAMBDA 365 UV/Vis (PerkinElmer) Spectrophotometer from 350 to 1100 nm, in an integrating sphere. The emission spectra were obtained using a modular spectrofluorometer, upon excitation of a continuous-wave NIR laser (970 nm, MDL-2W) focused on the sample to a spot size of 4 mm². The spectrometer is equipped with a detector (CCD, Short Focal Length Triple Grating Imaging Spectrographs, TRIAX 320 HORIBA) and an optical fiber. At ambient pressure, the NP powder was deposited on a silicon slice for better thermal transfer, the fluid was poured into a sapphire bowl closed with a glass lid for the emission acquisition. Data were collected after 10 s of temperature and laser stabilization, from 293 to 573 K (each 5 K) for the powder and from 298 to 423 K (each 5 K) for the fluid. The temperature was controlled using a thermo-cell (LINKAM Optical DSC600 cell).

Temperature calibrations under pressure were carried out using a high-pressure diamond anvil cell (DAC), as shown in Fig. S1 (ESI[†]), with a working hydrostatic pressure range of up to 1.3 GPa in Nycobase. According to the method described in previous work,⁹ the DAC (MDAC type BHP for Biology 100° symmetrical aperture, Betsa) consists of a 1.4 mm culet diamond anvil and a 400 mm thick diamond window, with a nickel gasket between them. The nickel gasket thickness was about 0.2 mm and comprises a hole of 0.5 mm in diameter.

The pressure inside the DAC was increased and maintained in the cell by inflating an internal membrane with helium. A heating ring (External Heating System, Betsa) was placed around the DAC for temperature regulation. A thermocouple inserted next to the metal seal in the DAC was used to measure the temperature of the sample with a precision of $\pm 0.1 \text{ K}$. During the experiments, a small amount of suspended sample ($< 1 \mu\text{L}$) was introduced into the hole in the seal. The hydrostatic pressure inside the DAC was determined by introducing ruby microparticles ($> 3 \mu\text{m}$) as a pressure sensor for calibration using their photoluminescence wavelength shift R1. These ruby microparticles were excited by a 460 nm laser. The wavelength position of the emission spectrum was referenced using an Argon lamp (Avalight-CAL-Mini) with a peak at 696.54 nm. The calibration of the hydrostatic pressure was based on previous literature.^{67,68} Based on previous work, the pressure uncertainty can be considered to be of the order of 0.05 GPa.⁹

2.3. Data analysis

Luminescence intensity ratio (LIR) calculation. The Er³⁺ thermometry is performed by the LIR variation in the function of temperature. According to the Boltzmann distribution, the population ratio of the two thermally coupled levels (TCLs) (N_{L2} and N_{L1}) varies with temperature following eqn (1).

$$\text{LIR} = \frac{N_{L2}}{N_{L1}} = \frac{I_{L2}}{I_{L1}} = \frac{g_2 \sigma_2 \omega_2}{g_1 \sigma_1 \omega_1} \exp\left(-\frac{(E_2 - E_1)}{k_B T}\right) = B \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (1)$$

where N_i denotes the population of excited ions, as the population of the energy level (N) is directly proportional to the emitted intensity (I), and I_i is thus the emitted intensity for a given level i . The pre-exponential constant B includes g_i , σ_i , and ω_i , which are the degeneracy, the effective emission cross-section, and the angular frequency of the transitions for a given level i , respectively. ΔE is the energy gap between the two TCLs, k is the Boltzmann constant, and T is the absolute temperature.³³ The emitted intensity was calculated by the integrated band area to average the total emitted intensities for each sublevel's transition.⁶⁹ The integrated area is estimated by MATLAB software according to Simpson's rule, from 540 to 567 nm for level L₁ (⁴S_{3/2} to ⁴I_{15/2}) and from 512 to 540 nm for level L₂ (²H_{11/2} to ⁴I_{15/2}) (Fig. S2, ESI[†]). ΔE can be then determined by the calibration curve of $\text{Ln}(\text{LIR})$ versus $1/T$. Moreover, S_R (relative thermal sensitivity), defined by eqn (2), is an important indicator of the reliability of the measurement.⁷⁰

$$S_R = \frac{1}{\text{LIR}} \times \frac{d(\text{LIR})}{dT} = \frac{\Delta E}{k_B T^2} \quad (2)$$

LIR experimental uncertainty determination. The intrinsic experimental uncertainty in the emission intensity ($\delta I/I$) is detector-dependent and is mainly determined by the value of the signal-to-noise ratio (SNR)⁷¹ (eqn (1), ESI[†]). The SNR of the CCD detector used for our measurement is stated by the manufacturer to be at best 0.05%. However, the detector operates with greater uncertainty, and, therefore, the $\delta I/I$ value is always higher than the indicated intrinsic SNR. The SNR is



estimated experimentally for each spectrum by dividing the baseline spectral fluctuation by the peak intensity (N_{L2} and N_{L1}). The experimental uncertainty is then determined by eqn (3).

$$\frac{\delta(\text{LIR})}{\text{LIR}} = \sqrt{\left(\frac{\delta I_1}{I_1}\right)^2 + \left(\frac{\delta I_2}{I_2}\right)^2} \quad (3)$$

3. Results

The results section will be divided into two parts. The first part deals with the characterizations of $\text{GdVO}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ powder and the second one with the characterizations of $\text{GdVO}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ dispersed at 0.5 wt% in a lubricant oil (Nycobase 5750).

3.1. Powder: $\text{GdVO}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ NPs

Structural characterizations. The crystalline phase of the synthesized nanoparticles $\text{GdVO}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ has been determined to be a pure tetragonal phase (JCPDC-17-0260) in our previous work (Fig. 1a).⁶² The SEM image of NPs $\text{GdVO}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ shows that the size of individual NP is about 30 nm (Fig. 1b). The TEM image (Fig. 2a) confirms that the particle size is of the order of 30 nm and shows the porosity of the particles induced by atomic diffusion during heat treatment. The HR TEM image (Fig. 2b) shows reticular planes 0.47 nm

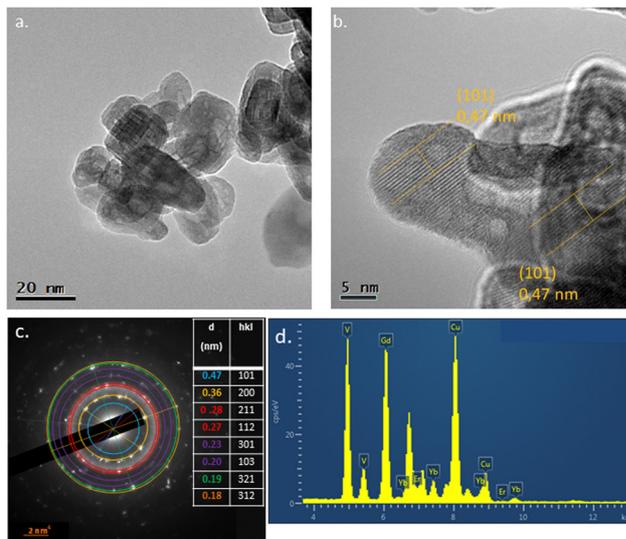


Fig. 2 TEM picture (a), HRTEM picture (b) electron diffraction pattern (c), and EDS spectrum (d) of $\text{GdVO}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ NPs powder.

apart, which is consistent with the plane distance (101) of GdVO_4 (JCPDS-17-0260). The electron diffraction pattern (Fig. 2c) confirms the presence of crystalline GdVO_4 (JCPDS-17-0260). Finally, the EDS spectrum (Fig. 2d) confirms the chemical composition of the probes, which contain Gd (28.9 at%), V (28.5 at%), Yb (4 at%) and Er (low content). This analysis leads to a Yb/Gd ratio of 0.14, consistent with the theoretical one (Yb/Gd = 0.10). The agglomerates formed by NPs size about 400 nm, which has been confirmed by TEM image,⁶² This result has also been observed in other's work.⁷²

Optical characterizations. Fig. 3a shows the powder absorption and emission (upon 970 nm excitation) spectra in blue and green lines, respectively. The $\text{GdVO}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ NPs powder absorbs a broad band of light in the NIR range, around 985 nm, due to the presence of the Yb^{3+} sensitizer of the Er^{3+} emitter. In the emission spectrum upon NIR laser excitation (970 nm), the NPs are able to emit green light (525 & 552 nm), from the Er^{3+} excited levels (${}^2\text{H}_{11/2}$ & ${}^4\text{S}_{3/2}$, respectively) to the ground state.^{28,72,73} The inset shows as well, that the powder emits strong green light when using a NIR laser pen. The proposed excitation mechanism is thus presented in Fig. 3b: upon excitation at 970 nm, Er^{3+} can be excited to the ${}^4\text{F}_{7/2}$ excited state by two sequentially absorbed photons (ground-state absorption (GSA) and excited-state absorption (ESA), respectively, indicated by the black dotted arrow).^{60,74–77} When Yb^{3+} is present in the system, the energy transfer between Yb^{3+} and Er^{3+} would occur mainly in the Er^{3+} excitation pathway. Since Yb^{3+} has a much larger absorption effective cross-section in the NIR region than Er^{3+} (${}^2\text{I}_{15/2}$ to ${}^4\text{I}_{11/2}$), the energy transfer upconversion process (ETU) becomes the main excitation of Er^{3+} to its upper levels (${}^4\text{F}_{7/2}$) to generate the same emissions. Other cross-relaxations and some backward energy transfer (EBT: Er to Yb) can also occur in this system,^{76,78–80} but they were not observed in our experiments. It is important to note that non-radiative relaxations are more noticed in the upconversion system,

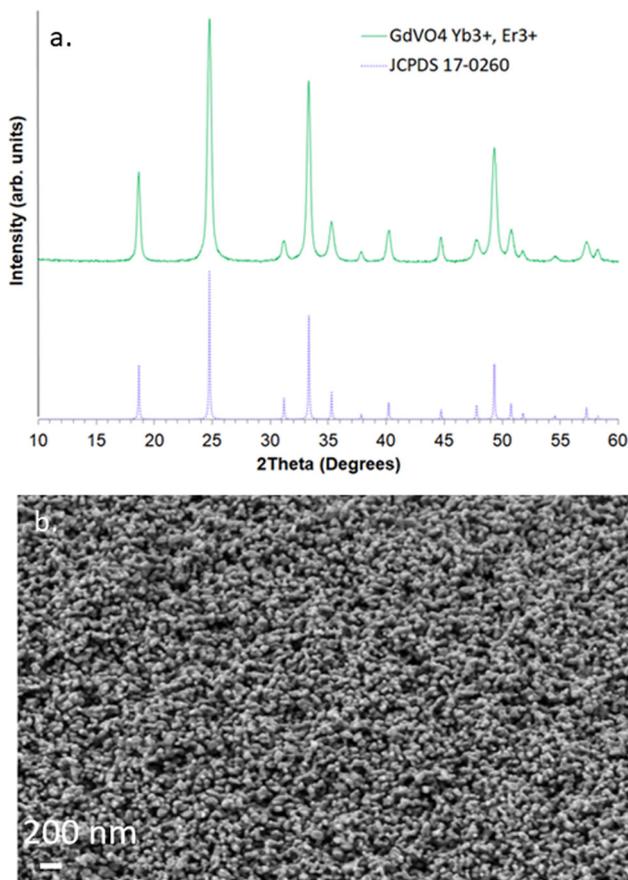


Fig. 1 XRD pattern (a) and SEM image (b) of $\text{GdVO}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ NPs powder.



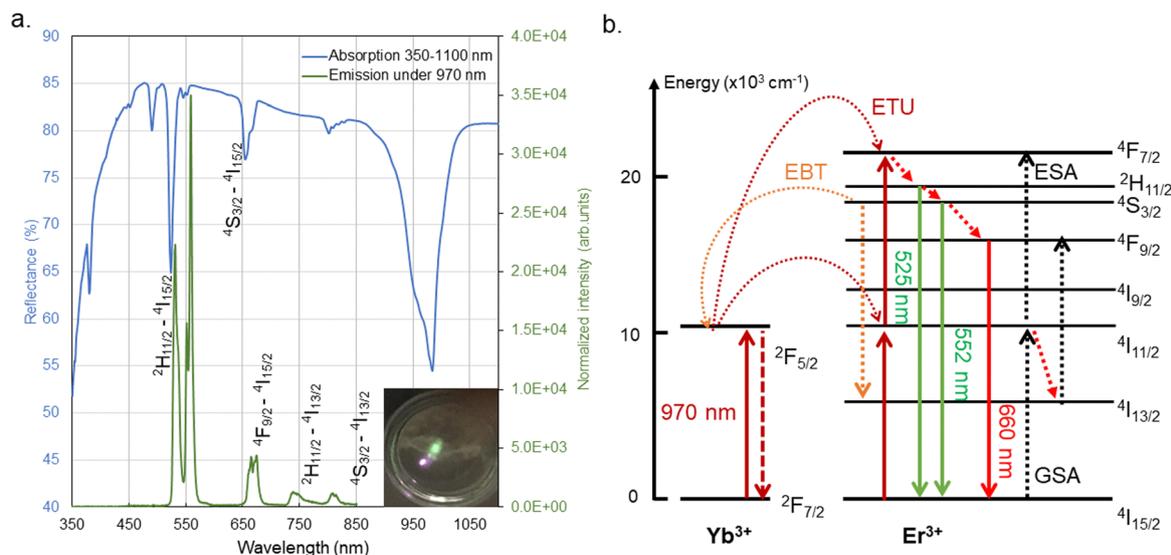


Fig. 3 (a) Absorption and emission spectra of the $\text{GdVO}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ powder sample. Inset: Photograph of the $\text{GdVO}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ powder sample with a 980 nm handheld laser pen. (b) The upconversion process between Er^{3+} and Yb^{3+} under NIR excitation.

which induces a non-negligible laser heating during high power density excitation. To prevent the laser-induced thermal effect from distorting the thermometric measurement, previous work⁶² has shown that the laser intensity should be less than 2.5 W cm^{-2} for NPs powder.

Temperature calibration by photoluminescence thermometry. The temperature was calibrated up to 573 K with the NPs powder under NIR laser at 2.5 W cm^{-2} . As shown in Fig. 4a, the intensity of peak λ_2 increases while peak λ_1 decreases with temperature. The ratiometric thermometry following the Boltzmann distribution was proven by the temperature calibration, with the LIR values varying with temperature (Fig. 4b). According to the Boltzmann eqn (1), $\text{Ln}(\text{LIR})$ is linearly proportional to $1/T$ up to 573 K, and more importantly, this variation is reversible. The slopes calculated by the fitted trendline of the calibration curves are used to estimate the energy gap (ΔE) in eqn (1). The average of the slopes is used to estimate ΔE (Table 1). The thermal detection efficiency was evaluated by calculating the relative thermal sensitivity S_R (eqn (2)), which was calculated with the average of the heating and cooling curves and is equal to $0.81\% \text{ K}^{-1}$ for the sample at 313 K. This value at low temperatures is close to the literature data (0.47 at 298 K ⁷³ and $1.11\% \text{ K}^{-1}$ at 307 K ⁸¹).

3.2. In suspension: $\text{GdVO}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ NPs

For further application in temperature measurement in tribology,⁹ an ester-based oil (Nycobase 5750) was chosen as the fluid medium to disperse $\text{GdVO}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanoprobles. Nycobase 5750 is used as a base oil for lubricant in tribological studies due to its suitable properties: rheological, high thermal resistance, chemical stability, and non-toxicity. The NPs were dispersed in the fluid and the suspension can be stable for more than 3 months. Furthermore, it was confirmed that Nycobase 5750 (Nycobase) does not absorb any NIR light.⁶² Thus, Nycobase can be considered as a good fluid medium for the upconversion

thermo-sensor, as it does not emit light upon NIR excitation and cannot be heated by the NIR laser.

Hydrodynamic size measurements. The NPs suspensions are prepared at different and relatively low concentrations: 0.1, 0.5, 0.75 and 1 wt% for DLS analysis. As shown in Fig. 5, the measured hydrodynamic size of the NP suspension after one week of settling. The hydrostatic size of the NPs aggregation is about 400 nm, which corresponds to the previous result observed in the TEM image.⁶² However, although in the 0.1 wt% suspensions, the hydrodynamic size is the smallest among all, around 100 nm, the second peak at 5000 nm shows that the suspension is not homogeneous. The position of the peak centroid, as well as the width of the peak, increases with concentration, which means that the hydrodynamic size increases while the monodispersity becomes more important with increasing concentration, respectively. Among the concentrations of 0.5, 0.75 and 1 wt%, the suspension at 0.5 wt% is the one that has both the smallest hydrodynamic size of NPs (less than 350 nm) and the best monodispersity. It is important to note that the monodispersity and small size of nano probes are required for tribological applications to improve the spatial resolution.

Rheological properties characterizations. Since it is essential to preserve the rheological properties of Nycobase as much as possible for further friction tests, the viscosity of 0.5 wt% suspensions is measured at different temperatures with pure Nycobase as a reference. Fig. 6 show the measured viscosities of 0.5 wt% and the reference of pure Nycobase at 293 to 373 K, respectively. As pure Nycobase is a Newtonian fluid, its viscosity will not change with the shear rate, which is thus presented in line in Fig. 6. The difference in viscosity between the 0.5 wt% suspensions and the pure Nycobase ($<2.97\%$) can hardly be observed in the experimental uncertainty range ($<5\%$). Moreover, at 293 K, under a high shear rate ($>8000 \text{ s}^{-1}$), the viscosity decreases very slightly with increasing shear rate for both suspensions and pure Nycobase, which is explained by the shear-induced heating effect that decreases viscosity.⁸



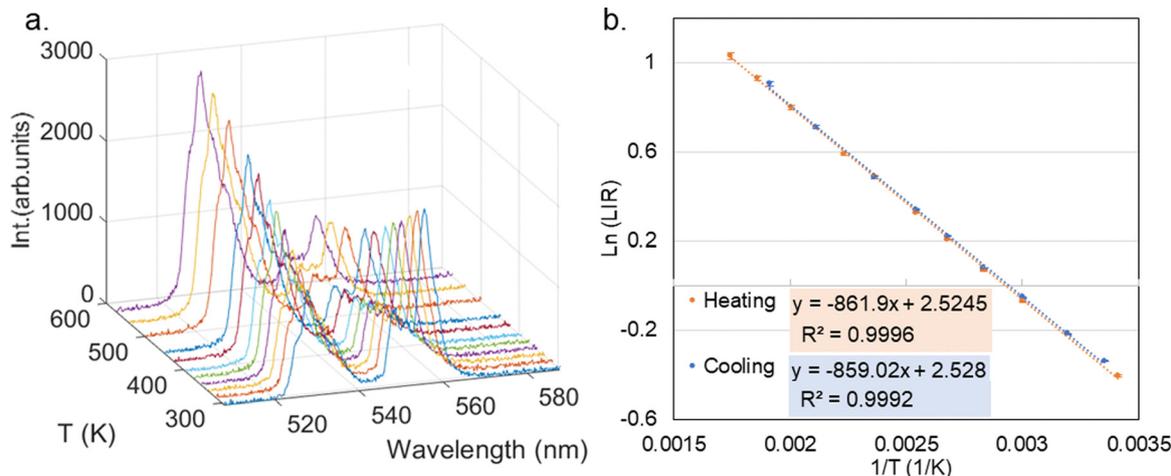


Fig. 4 GdVO₄:Yb³⁺/Er³⁺ powder upon NIR laser at 2.5 W cm⁻²: (a) emission spectra at 293–573 K. (b) Temperature calibration curve and fitted trendline equations, error bars determined by uncertainty (eqn (3)).

Table 1 The estimated energy gap (ΔE) and the uncertainty of temperature calibration curves

	Y offset	B	Slope	$\Delta E_{\text{estimated}}$	$\delta(\text{LIR})/\text{LIR}$ (average) (%)
NPs powder	2.5263	13	-860.46	598	1.92
NPs in suspension	2.4839	12	-925.12	643	19.97
NPs suspension (P_{constant})	2.6395	14	-897.98	624	14.18
NPs suspension (P_{varying})	2.5697	13	-870.38	605	12.84

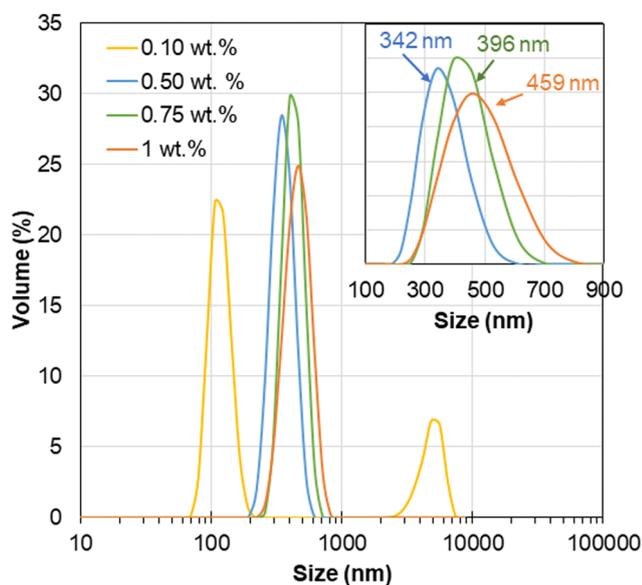


Fig. 5 The DLS diagram of GdVO₄:Yb³⁺/Er³⁺ suspension at 0.1, 0.5, 0.75 and 1 wt%.

The viscosity of the 0.5 wt% NPs suspension varies almost in the same way as that of the pure Nycobase fluid. Thus, the dispersion of the NPs does not affect the rheological properties of the Nycobase in the temperature and shear rate range studied, which is

a crucial condition for using the NPs suspension as a lubricant. This means that the presence of GdVO₄:Yb³⁺/Er³⁺ nanoprobles at 0.5 wt% in the fluid will not change the tribological contact behavior. More importantly, for the 0.5 wt% NPs suspension, it has been verified that there is no impact of NIR laser heating even at high laser intensity in our previous work.⁶² Therefore, the 0.5 wt% GdVO₄:Yb³⁺/Er³⁺ nanoprobles suspension has been selected for further temperature calibration under atmospheric and under high pressure (up to 1.1 GPa) in the further study.

Temperature calibration under atmospheric pressure. Temperature calibration by upconversion emission was performed on the NPs suspension between 298 and 423 K (Fig. 7a). The maximum temperature was limited to avoid possible evaporation of Nycobase during the measurement. At 0.5 wt% of NPs, the emission of the suspension could be measured at a high pump power density (13.5 W cm⁻²). However, the calculated uncertainty (eqn (3)) cannot be negligible and has been represented on the calibration curve by an error bar. Although the spectral

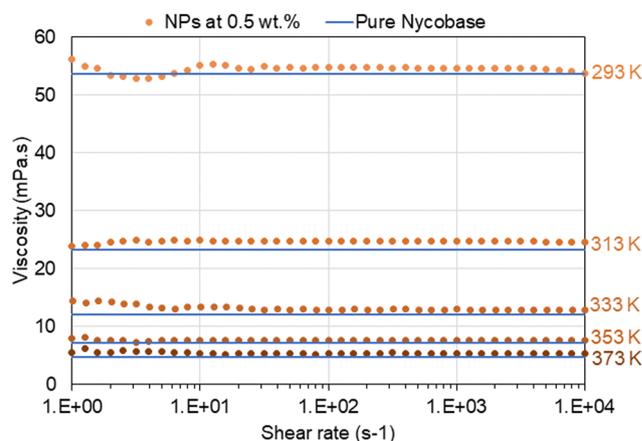


Fig. 6 Viscosity of GdVO₄:Yb³⁺/Er³⁺ NPs suspension at 293–373 K under a shear rate of 1–10⁴ s⁻¹ for 0.5 wt% NPs suspension (in dot) and pure Nycobase (in line).



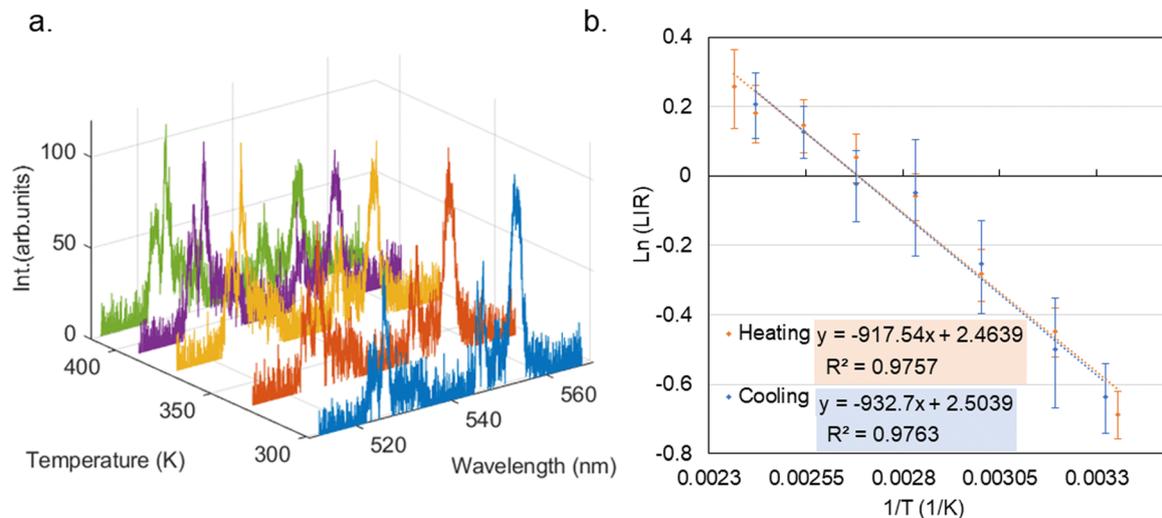


Fig. 7 $\text{GdVO}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ suspended at 0.5 wt% upon NIR laser at 13.5 W cm^{-2} : (a) emission spectra at 298–423 K. (b) Temperature calibration curve and fitted trendline equations, error bars determined by uncertainty (eqn (3)).

uncertainty is notable, the temperature calibration curve of the 0.5 wt% NPs $\{\text{GdVO}_4\text{:Yb}^{3+}/\text{Er}^{3+}\}$ is linear and reversible up to $150 \text{ }^\circ\text{C}$, with little deviation between the heating and cooling curves (Fig. 7b). The energy gap (ΔE) was then fitted by the curves in Table 1, and the relative sensibility (S_R) is $1.17\% \text{ K}^{-1}$ at 313 K, which is consistent with the values obtained with the powder calibration curve.

Temperature calibration under high pressure. In order to apply the NPs suspension as a thermo-sensor lubricant for temperature measurement in tribological friction experiments, the photoluminescence thermometry of the suspension was studied under pressure (up to 1.1 GPa) in a diamond anvil cell (DAC) at every 20 K from 293 K to 353 K, under a 13.5 W cm^{-2} NIR laser as in the previous experiments. To study the effect of pressure on the LIR of NPs, two sets of data were collected in the DAC under isothermal conditions. The first group, called P_{constant} , is a repeated measurement at the same temperature and pressure (the lowest pressure for the corresponding temperature). The second group, called P_{varying} is a sequence of

measurements at a given temperature for a variable pressure. The emission spectra are presented in Fig. 8a at varying temperatures and constant pressure ($P = 0.6 \text{ GPa}$), showing that increasing temperature increases the emission intensity of peak λ_2 and decreases that of the peak λ_1 . Conversely, Fig. 8b shows the negligible change in emission intensity under varying pressure at a constant temperature. Besides the LIR measurement, the peak shift has been verified for peak 1 (at 553 nm). As shown in Fig. 9, the corrected peak shift is not significant ($<0.2 \text{ nm GPa}^{-1}$) at a given temperature under varying pressure.

As shown in Fig. 10a, $\text{Ln}(\text{LIR})$ under P_{constant} is plotted by a hollow point for each temperature, and $\text{Ln}(\text{LIR})$ under P_{varying} is plotted by a solid symbol for each temperature as well. The LIR value under P_{constant} and P_{varying} does not change with increasing pressure but only with temperature. An analysis of variance is conducted to conclude the influence of pressure on the LIR variation. In Table 2, the variance (VAR) at P_{constant} (here the residual variance) and that at P_{varying} (here the explained

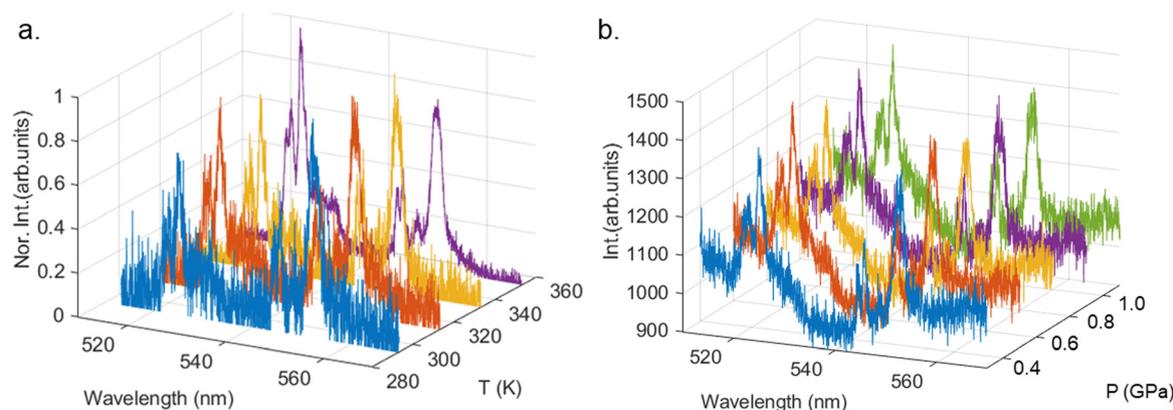


Fig. 8 $\text{GdVO}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ suspended at 0.5 wt% in DAC upon NIR laser at 13.5 W cm^{-2} : (a) emission spectra at 293–353 K under 0.6 GPa; (b) emission spectra at 313 K under 0.4–1.1 GPa.



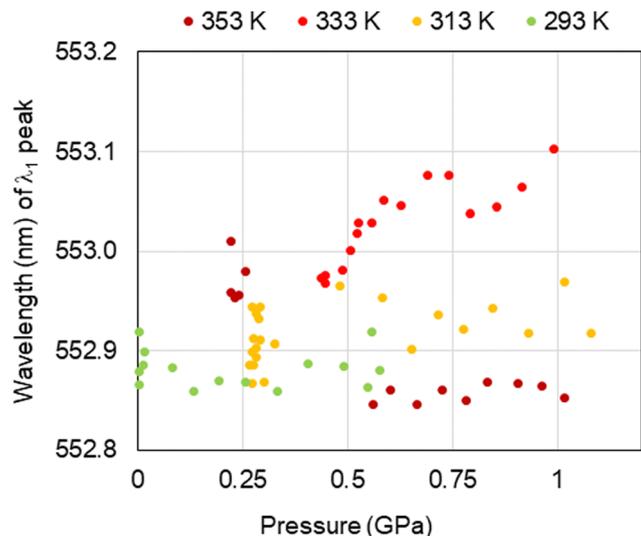


Fig. 9 GdVO₄:Yb³⁺/Er³⁺ suspended at 0.5 wt% in DAC upon NIR laser at 13.5 W cm⁻²: λ₁ peak position (corrected) under pressure at different temperatures.

variance) are calculated for each temperature. The uncertainties calculated by SNR of emission spectra are listed. The VAR(P_{varying}) is always lower than the VAR(P_{constant}). This means that the distribution of the LIR value is less dispersed when the pressure varies than when the pressure is constant. This means that the pressure has no effect on the LIR variation. To confirm this result, the ratio VAR(P_{varying})/VAR(P_{constant}) was calculated and found to be less than 1. This result shows that the slight change in the LIR value under isothermal conditions cannot be explained by the variation in pressure. Then, the LIR value is independent of pressure (up to 1.1 GPa) in the temperature range studied.

Therefore, the thermometric validity of NPs suspended under pressure was investigated by averaging Ln(LIR) under P_{constant} as well as P_{varying} for each temperature. As shown in

Fig. 10b, the temperature calibration curve under both P_{constant} and P_{varying} is linear as a function of $1/T$ and overlap with each other. $\Delta E_{\text{estimated}}$ by their slopes is therefore very close, 624 and 605 cm⁻¹ respectively (Table 1). This observation confirmed that the LIR of suspended NPs GdVO₄:Yb³⁺/Er³⁺ is independent of pressure (up to 1 GPa), and therefore, the NPs are able to measure temperature by their emission without any effect caused by pressure variation.

To summarize, if we compare the temperature calibration curve at the same laser pumping power (13.5 W cm⁻²) of the 0.5 wt% NPs suspension in our previous results (Table 1), the $\Delta E_{\text{estimated}}$ obtained by the slope of the calibration curve could be considered as the same, which confirms the reliability of these NPs GdVO₄:Yb³⁺/Er³⁺ for temperature measurement under a pressure up to 1 GPa. The uncertainty of the measurement depends on the intensity of the emission, the quantity of NPs in the suspension being much less important than in the powder, the uncertainty has become important in the suspension. Nevertheless, in the NPs suspension under atmospheric pressure, the 19% uncertainty caused only a 7.5% error in the $\Delta E_{\text{estimated}}$ value compared to the NPs powder. It is important to note that the configuration of the optical experiments is different between the temperature calibration under pressure in the DAC and at atmospheric pressure with a thermal controller, which may imply differences in the illuminations and therefore uncertainty in the emission intensity, and consequently, in the LIR value. This may be the reason for a slight shift in the constant B in the Boltzmann equation. However, once the ΔE is consistent with the previous result, the GdVO₄:Yb³⁺/Er³⁺ NPs can be validated as thermometric and pressure-independent probes.

4. Conclusions

A non-contact, pressure-independent nanothermometer was investigated for tribological temperature measurement using

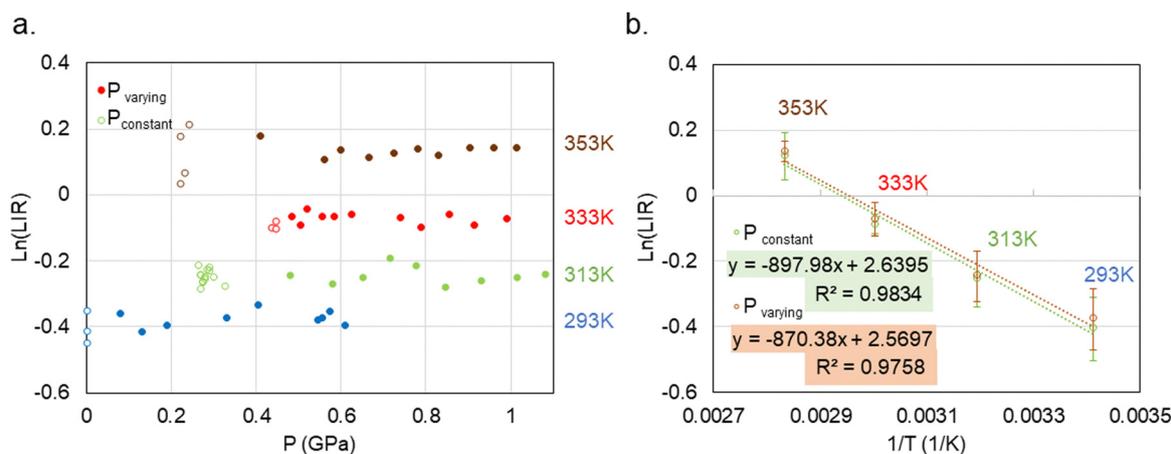


Fig. 10 GdVO₄:Yb³⁺/Er³⁺ suspended at 0.5 wt% upon NIR laser at 13.5 W cm⁻²: (a) distribution of Ln(LIR) values at four temperatures (293 to 353 K) under constant pressure (hollow point) and pressure varying up to 1.1 GPa (solid point). (b) Temperature calibration curve and the fitted trendline equations under constant pressure (green) and pressure varying (brown), error bars determined by the standard deviation of overall data.



Table 2 The average of LIR and variance of LIR for each temperature in DAC

T (K)	P_{constant}			P_{varying}			VAR ratio ^a
	P (GPa)	SNR (%)	VAR	P_{max} (GPa)	SNR (%)	VAR	
293	0.01	6.47	2.54×10^{-3}	0.61	6.48	6.30×10^{-4}	0.25
313	0.29	6.55	5.27×10^{-4}	1.08	5.97	5.00×10^{-4}	0.95
333	0.45	2.74	2.92×10^{-4}	0.99	4.22	2.81×10^{-4}	0.96
353	0.23	8.28	7.49×10^{-3}	1.02	3.47	4.06×10^{-4}	0.05

^a VAR ratio: the ratio of VAR P_{varying} /VAR P_{constant} .

GdVO₄:Yb³⁺/Er³⁺ upconversion nanoparticles. The NPs were prepared by precipitation and thermal treatment. The NPs dispersed in the fluid lubricant has the same photoluminescence thermometric properties as the NP powder. At low NP dispersion concentration, the suspension retains the original rheological properties of the lubricant even at a high temperature (373 K) and at a high shear rate (10^4 s^{-1}). In order to apply the NPs in frictional contact for temperature sensing, temperature calibration was performed under hydrostatic pressure (up to 1.1 GPa) in a diamond anvil cell. The result confirmed the independence of the LIR from pressure, and the calibration curve under variable pressure is superimposed on that under constant pressure. Therefore, the incorporation of these GdVO₄:Yb³⁺/Er³⁺ nanosensors into the lubricant leads to the formation of a suspension that allows temperature measurement by the LIR method without being disturbed by the influence of pressure. The next step is the application in tribological contact, in particular in fluid lubrication.

Author contributions

C. J., L. B., D. P. and S. D. are the supervisors of projects. Y. Z., L. B. C. J. and D. P. performed the experiments. G. L., D. P., N. B., M. M., Y. M., C. D, F. C. and D. F. provided input into the design of the experiments. Y. Z., G. L., L. B., N. B., D. P. and S. D. co-wrote the manuscript with input from other authors.

Conflicts of interest

There are no conflict to declare.

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