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RESEARCH ARTICLE

# Boltzmann constant determined by fluorescent spectroscopy for verifying thermometers

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**Abstract** As is always accompanying temperature in physics fundamental principles, Boltzmann constant $k_B$ can be used to verify the accuracy of a thermometer. This paper presents a photoluminescent method to measure $k_B$ via temperature dependent fluorescence of phosphors. Diagram of a phosphor's energy levels was simplified to illustrate the principle of measurement. The relationship between $k_B$ and $h*c$ (Planck constant $h$ multiplying light speed in vacuum $c$) was experimentally derived. Finally, the determined $k_B$ was $1.38065 \times 10^{-23}$ J/K. The determination could give a value of $(1.38\pm0.1) \times 10^{-23}$ J/K even when the in-use spectrometer was with a poor resolution as about 2 nm. At the end, optimization of measuring conditions for the determination process was suggested.

**Keywords** temperature, Boltzmann constant ($k_B$), Planck constant ($h$)

## 1 Introduction

Temperature always ($T$) appears as thermal energy $k_BT$ ($k_B$ is Boltzmann constant) in fundamental laws of physics. The interest in the measurement of $k_B$ has arisen in recent years, desiring an employment of the accurate $k_B$ value in the quantum definition of the basic unit of temperature-"Kelvin (K)" [1]. However, rather than the metrologic application, a less precise measurement of the constant can be used to verify the accuracy of an industrial thermometer. This operation could be quite easy and convenient with a fluorescent spectroscopy test.

Metrologists have developed several high accurate methods to fix the value of $k_B$. Recent progress of different measurement methods [1] focuses on noise thermometry, Doppler broadening thermometry, dielectric constant gas thermometry, and acoustic gas thermometry. Therein, a relative uncertainty of $3.8 \times 10^{-5}$ was given by optical absorption line profile analysis which was based on Doppler broadening principle [2,3]. All these laboratory works require scientific apparatus and sophisticated operating skill. Then, while one is seeking a quantum method for in-situ/real-time verifying his thermometer in a production line, a cheaper, more convenient, and probably less precise method could be preferred. Also such an economical method may find its way in college experiments for students.

In this paper, a fluorescent spectroscopic method was introduced. Population of electrons in thermal coupled levels of phosphors can be described with Boltzmann's distribution. Based on temperature dependent photoluminescence of a phosphor, the Boltzmann constant $k_B$ was determined by the relationship between measured relative intensity and temperature. The experimental setup is high compact and the engaged devices are easily available on the market. The manipulation of the setup requires not much skill or technical training. Even so, accompanying a relatively large uncertainty, the measured result is well consistent with the value recommended by the Committee on Data for Science and Technology (CODATA) [4] in 2010.

## 2 Experiments

Phosphor $Y_2O_3$:Er,Yb was prepared by liquid combustion method [5]. The aqueous solutions of rare earth nitrates and glycin were dried and then heated to self-igniting, after they were mixed. The residual powders were the desired phosphors. The doping concentration of $Er^{3+}$ is 2 mol% and that of $Yb^{3+}$ is 0.5 mol%. The particle size is about 200 nm.

The phosphor's luminescence was analyzed with a model WDS-3 spectrometer under the excitation of a continuous wave laser diode (LD) at 980 nm. The

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spectrometer has a focal length of 0.3 m. The phosphor was glued on a hot plate, where temperature was monitored and controlled by a thermometer with K-type thermocouple. The thermometer precision is ±1°C.

## 3 Methodology of determination

The theory of determining $k_B$ evolves from a temperature probing technology naming fluorescent intensity ratio (FIR) technology [6]. The principle can be illustrated with a simplified diagram of energy levels (Fig. 1). Denoted with levels 2, 1 and 0, $^2H_{11/2}$, $^4S_{3/2}$ and $^4I_{15/2}$ of $Er^{3+}$ energy levels are selected.

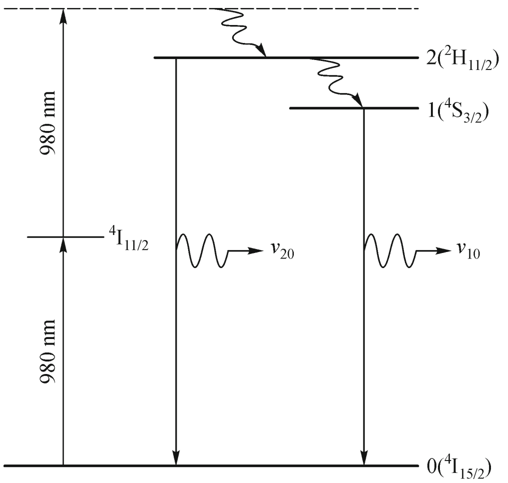

**Fig. 1** Selected energy levels of $Er^{3+}$ for the determination of Boltzmann constant

Spontaneous transition takes place from levels 2 and 1 to level 0. The emission intensity $I_{ij}$ ($i = 2, 1, j = 0$) relates to the spontaneous transition probability $A_{ij}$, the frequency of emission light $v_{ij}$, and the population $N_i$ of state $i$ ($i = 2,1$):

$$I_{ij} \propto A_{ij} \nu_{ij} N_i. \tag{1}$$

Then the intensity ratio $R$ of transitions of state 2 to state 0 on state 1 to state 0 is

$$R = \frac{I_{20}}{I_{10}} = \frac{A_{20}\nu_{20}N_2}{A_{10}\nu_{10}N_1}. \tag{2}$$

As levels 2 and 1 are close to each other, they are thermal coupled. At thermal equivalent state, population ratio $N_2/N_1$ follows the Boltzmann's distribution:

$$\frac{N_2}{N_1} = \exp\left(\frac{-E_{21}}{k_B T}\right), \tag{3}$$

where $T$ is temperature (unit: K), and $E_{21}$ is the energy gap between levels 2 and 1. For the phosphor, the mentioned transitions take place in 4f levels of the $Er^{3+}$ ion. As all the 4f electrons are shielded by the 5d electron shell in the rare earth ions, energies $E_{20}$ and $E_{10}$ are not obviously dependent on environmental temperature, meaning also that $E_{21}$ is almost constant. Normally, the thermal coefficient of a 4f level's shifting is less than 0.02 cm$^{-1}$/K, and simultaneous shift of levels is another cause of constant energy gap between the levels. The invariability can be directly observed in the emission and/or excitation spectra.

The total probability of spontaneous transitions is under the influence of temperature. However, the branches ($A_{ij}$) are jointly affected. When the branches are normalized with the total probability, it is the rare earth ion's site symmetry which decides the transition probabilities $A_{ij}$ of the ion. As is in a narrow range of temperature, site symmetry of the ions in a cubic yttria is out of the influence of thermal expansion and then remains unchanged. Hence, the transition probabilities $A_{ij}$ are conditionally constant.

Combine Eq. (3) with Eq. (2), there is

$$R = C_1 \exp\left(\frac{-E_{21}}{k_B T}\right), \tag{4}$$

where $C_1$ is a constant for a certain material, taking account of the constant $E_{20}$, $E_{10}$ and $A_{ij}$.

With logarithmic operation on Eq. (4) , it transforms into

$$\ln R = \ln C_1 - \frac{E_{21}}{k_B} \cdot \frac{1}{T}. \tag{5}$$

Hence, by measuring spectra at various temperatures, value of $E_{21}$ can be derived from the emission spectra via $E_{21} = E_{20} - E_{10} = h(\nu_{20} - \nu_{10}) = hc(1/\lambda_2 - 1/\lambda_1)$. Then plotting curve of $\ln R \sim 1/T$, $k_B$ can be finally determined by the slope $s$ of $\ln R \sim 1/T$ fitting line:

$$k_B = -\frac{E_{21}}{s}. \tag{6}$$

## 4 Results and discussion

Emission intensity of $Y_2O_3$:Er,Yb and relative intensity of the emission peaks are temperature dependent (Fig. 2). That is to say, peaks descend with varying degrees under the same change of temperature. Emission of transitions $^2H_{11/2}$, $^4S_{3/2}$ to $^4I_{15/2}$ is in the range of 510–570 nm, accordingly about 19600–17550 cm$^{-1}$. When peaks 1 and 2 from $^4S_{3/2}$ and $^2H_{11/2}$ respectively are selected, the intensity ratio of peak 1 to 2 varies from 2.36 to 1.66 as the temperature is from room temperature to 51°C, and the energy gap $E_{21}$ between the two thermal coupled levels is read out as 810.8 cm$^{-1}$ from the emission spectra.

Foregoing theoretical analysis has linked Boltzmann constant $k_B$ to Planck constant $h$ and the speed of light $c$ in vacuum. Based on the theoretical analysis, Fig. 3 is plotted

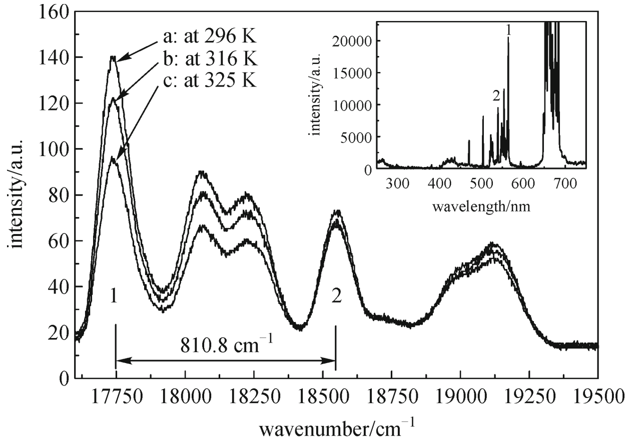

**Fig. 2** *In situ* emission of $Y_2O_3$:Er,Yb at various temperature, pumped at 980 nm. Inset: $Y_2O_3$:Er,Yb emission in visible range at room temperature

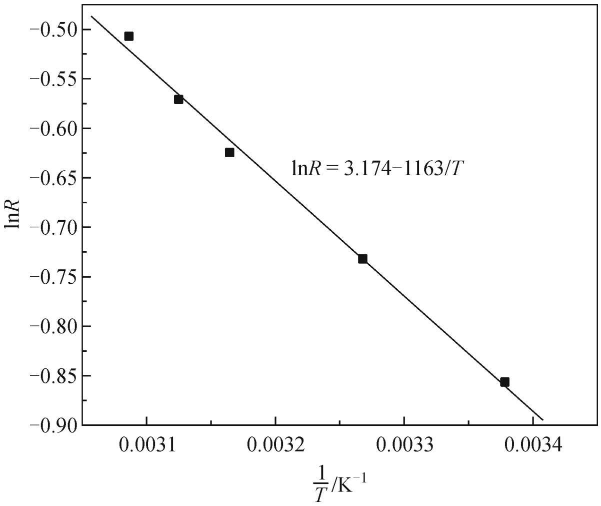

**Fig. 3** Dependence of $Y_2O_3$:Er,Yb fluorescent intensity ratio ($I_2/I_1$) on temperature, where intensities $I_2$ and $I_1$ are respectively heights of peaks 2 and 1 in Fig. 2

with reciprocal of the temperature $1/T$ as abscissa and the logarithm of intensity ratio $\ln R$ as ordinate. Slope ($s$) of the fitting line is $s = (-1163\pm130)$ K.

Light speed in vacuum is defined as an exact value $c$ = 299792458 m/s, recommended Planck constant by CODATA is $h$ = 6.62606957(29) × $10^{-34}$ J·s. Then Boltzmann constant $k_B$ is determined as

$$k_B = (1.38 \pm 0.1) \times 10^{-23} \mathrm{J/K}.$$

The recommended Boltzmann constant $k_B$ by CODATA in 2010 is $k_B$ = 1.3806488(13) × $10^{-23}$ J/K. Our experimental result is well compliant with the recommended value. In other words, even though our result is with a much large uncertainty originated from the poor resolution of the in-use spectrometer and the limited amount of data plot in the investigated narrow temperature range, the value of determined $k_B$ is somehow accurate. By the way, foregoing analysis also answered the question raised by Danenhower [7], who tried to extract the interdependence of Boltzmann constant ($k_B$), Planck constant ($h$) and light speed in vacuum ($c$) via blackbody radiation but gave no conclusion.

The determination process could also employ other transition peaks, for example, emission peaks of $Er^{3+}$ at 523 and 548 nm. The corresponding calculation will give almost the same result as above. However, overlap of multiple peaks leads to difficulty in locating the peaks' position and calculating the intensity ratio. Normally we selected isolated peaks in the fluorescent spectra to minimize the reading uncertainty of peak intensity and peak position.

Relative uncertainty of the determination can be estimated via:

$$\frac{\mathrm{d}k_B}{k_B} = -\frac{\mathrm{d}h}{h} - \frac{\mathrm{d}c}{c} - \frac{\mathrm{d}(\nu_2-\nu_1)}{\nu_2-\nu_1} + \frac{\mathrm{d}s}{s}, \qquad (7)$$

where $\mathrm{d}h/h = 4.4 \times 10^{-8}$, and $\mathrm{d}c/c = 0$ [4]. Reading error of the energy gap and error of the fitting slope mainly decide the total uncertainty of final determination of $k_B$. The item $\mathrm{d}s/s$ can be lowered by a larger number of fitting points (temperature points) and accurate intensity monitoring. Then the left factor is the accuracy of the reading wavenumbers $\nu_{20}$ and $\nu_{10}$. That means that scanning repeatability and spectral resolution of the employed spectrometer is magnificently important for accurate/precise determination of the constant $k_B$. In our experiment, the spectrometer is a low resolution one, and then the determination uncertainty is not satisfactory enough. However, when supposing a spectrometer instead with a repeatability of 0.001 $\mathrm{cm}^{-1}$ in the scanning range and resolution less than 0.1 $\mathrm{cm}^{-1}$ at 550 nm, the relative uncertainty of the determination can be expected to be small as 1.3 × $10^{-6}$, near the relative standard uncertainty of $k_B$ (9.1 × $10^{-7}$) from the CODATA [4]. Experiments with higher spectral resolution and more accurate temperature control are under way.

Various authors have done works on temperature sensing with optical spectroscopy (see Table 1). When the FIR technology was used, we can also extract Boltzmann constant $k_B$ from the reported data [8–15]. Again, the average value 1.3795 × $10^{-23}$ J/K is very close to the recommended value, and the difference is only 0.08%. The results prove FIR technology a quite confident method for determination of Boltzmann constant $k_B$. It is also possible to retrieve the physics constant from Raman spectrum, where the intensity ratio of stokes to anti-stokes lines plays the role.

It seems that larger energy gap enables more proximate determination to known Boltzmann constant $k_B$. This can be easily understood with regarding to Eq. (7). While the

**Table 1** Boltzmann constant determined by optical spectroscopies

| Ref. | technology | energy gap $E_{21}$/cm$^{-1}$ | fitting slope $s$/K | $k_B$/($10^{-23}$ J·K$^{-1}$) |
|---|---|---|---|---|
| [3] | Doppler broadening | – | – | 1.38065(26) |
| [8] | Raman spectrum | Phonon energy $\hbar\omega$ | $\hbar\omega/k_B$ | – |
| [9] | FIR technology | 700 | 1015 | 1.3700 |
| [10] | FIR technology | 719 | 1035 | 1.3800 |
| [11] | FIR technology | 872.3 | 1255.14 | 1.3805 |
| [11] | FIR technology | 953.1 | 1371.51 | 1.3804 |
| [12] | FIR technology | 800 | 1152 | 1.3795 |
| [13] | FIR technology | 390 | 559 | 1.3859 |
| [14] | FIR technology | 681 | 981 | 1.3790 |
| [15] | FIR technology | 896 | 1289.09 | 1.3807 |
| average of the FIR determination = 1.3795±0.0044 | | | | |

measurement uncertainty of energy gap $d(v_2 - v_1)$ is similar, larger gap depth $(v_2 - v_1)$ results in less relative uncertainty $d(v_2 - v_1)/(v_2 - v_1)$. This item decides less relative uncertainty of the determined item $dk_B/k_B$.

Temperature control is important in the experiment. The measuring accuracy might be affected by the temperature rising of the phosphor under dense excitation. Laser heating effect has to be avoided during temperature calibration. Pulsed laser may be a good choice to eliminate heating effect. Anyway, adequate heat exchange between phosphor and its environment is essential. And vice versa, an obvious discrepancy in the determined constant and the suggested one is definitely a symbol of malfunction of a thermometer. This makes the FIR technology a diagnostic tool for various thermometers.

For the purpose of determining Boltzmann constant $k_B$, the suitable temperature range (for efficient thermal coupling of levels) can be derived from a rough estimation $3k_BT/2 \geqslant E_{21}$. Normally the range of 200–450 K is good for experiments on $Eu^{3+}$, $Er^{3+}$, $Yb^{3+}$, $Nd^{3+}$ or other rare earth doped phosphors. The temperature quenching effect would not affect the principle of determination much for these ions. This range is easily available when using a cascaded Peltier device and a hot plate.

## 5 Conclusions

In conclusion, this paper reports fluorescent spectra methods to determine Boltzmann constant $k_B$. The obtained relationship between Boltzmann constant $k_B$ and Planck constant $h$ and light speed in vacuum $c$ reveals basic physical relation between temperature $T$ and frequency $v$ (or time), as both $k_BT$ and $hv$ appear as energy. Experimentally determined Boltzmann constant $k_B$ is well consistent with the value recommended by the CODATA. Very low uncertainty of determination can be expected on suggested spectrometer. Temperature range for the determination is also suggested. The determination method could have a potential application in verifying commercial thermometers.

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