

PHOSPHOR THERMOMETRY TECHNIQUES FOR THE REALIZATION OF THERMAL STANDARDS*

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ABSTRACT

The possibility of using single-crystals of thermographic phosphors in a new realization of the degree kelvin has been explored. The experimental technique would involve the laser-induced fluorescence of a rare-earth-doped phosphor, the optical decay lifetime of which would be measured relative to an atomic clock, in order to obtain a primary standard of temperature based only on atomic quantities. In principle the technique could provide the first realization of the kelvin over continuous ranges of temperature, without the need for interpolation between fixed thermodynamic transition points. Possible experimental arrangements for carrying out such a realization of the degree kelvin will be discussed.

INTRODUCTION

Thermometer calibrations at all standards laboratories are carried out within the context of the International Temperature Scale of 1990 (ITS-90). This temperature scale is maintained between the values of 13 °K and 1234 °K in terms the well-defined thermodynamic transition points (melting, freezing, vapor pressure and triple points) of several pure materials, including the gases hydrogen, neon, oxygen and argon, and the metals mercury, gallium, indium, tin, zinc, aluminum and silver, as well as with water (1). The base unit of the SI system associated with the measurement of thermodynamic temperature, the degree kelvin, is defined as 1/273.16 of the thermodynamic temperature of the triple point of water (2). It is realized via interpolation over sub-ranges of the ITS-90 span, with calibration errors on the order of a few tenths of a millikelvin propagating from it. The structure, maintenance and improvement of the ITS-90 is made possible by a massive effort on the part of many physicists, chemists

and metrologists at national standards laboratories around the world, all of whom contribute to the quest for lower overall uncertainty in the realization of the degree kelvin via this scale. The ITS-90 is disseminated to industry by a variety of primary, secondary and transfer-standard thermometers. The overall realization and use of this temperature scale is thus intricately dependent on a wide variety of material artifacts, devices and interpolative algorithms, with no direct tie to atomic quantities that might be independent of such dependencies. The other base unit of the SI system for which a similar situation holds is the kilogram. At present the international prototype for it is a platinum-iridium mass preserved at the International Bureau of Weights and Measures in France. To realize the kilogram and disseminate its value, many similar such masses are intercompared with each other (and occasionally with the international prototype) during the course of several complex series of precision weighings. The mass standards of individual laboratories can then be calibrated against the kilogram “as maintained” at each of the various national standards laboratories. See, for instance, reference (3) for further details of that process.

Ideally, *all* of the base units of the SI system would be realized in terms of atomic quantities that are independent of artifacts. The units could then be established with essentially equal precision at any laboratory anywhere. Indeed, great effort is being expended on research into the realization of the kilogram on the basis of building it from single crystals of pure silicon, the atomic planes of which are regular enough in form and structure to permit single-atom counting and summation. Our purpose here is to propose something similar in terms of the realization of the degree kelvin. By measuring the laser-induced fluorescence lifetimes of very regular single crystals of rare-earth-doped ceramic oxides and/or oxysulfides in terms of the “ticks” of an atomic clock, one could in principle establish a new kind of temperature scale tied directly to atomic constants from which the degree kelvin could be realized and disseminated, possibly with improved precision. In what follows we describe the critical features of the proposed technique and discuss some preliminary attempts at achieving demonstration of a prototype.

PROPOSED TECHNIQUE

Remote thermometry via thermographic phosphors has been explored in depth over the past 20 or so years, and a large number of applications for this methodology have been described in the literature (4). The existence of charge-transfer states in materials such as $\text{Y}_2\text{O}_3:\text{Eu}$ and $\text{La}_2\text{O}_2\text{S}:\text{Eu}$ provides for a temperature-dependence in the amplitudes and exponential decay lifetimes of laser-induced fluorescence in such materials, with the excitation energy being shared between radiative (photon) and nonradiative (phonon) de-excitation processes. See (5) for a reference to a thorough listing of several candidate materials that exhibit this type of behavior. The physics underlying the temperature-dependence of the ratio between these de-excitation mechanisms is reasonably well understood and useful models exist for the quantum mechanics of the decay rates (4). If satisfactory predictions of temperature vs. decay rate can be made for an appropriate material, and if the subsequent experimentally measured decay rates could be determined using an apparatus that has a cesium beam atomic clock as its time base, then the essential features are in place for realizing a temperature scale in terms of atomic quantities. The general components of an experimental arrangement for accomplishing this type of measurement are shown in Figure 1. A tunable dye laser or some other suitable excitation source is used to optically pump the phosphor sample which is located inside an (ideally) gradient free furnace. The fluorescence signal is detected by a fast, low-noise photodetector and a waveform-processing oscilloscope and/or off-

line computer is used to analyze the signal and extract the exponential decay-time constant. The time base for the whole system would be a cesium beam atomic clock or, possibly, a suitable stable signal derived from one (such as the U.S. NIST WWV radio signal). Given a satisfactory theoretical understanding of the relationship between the temperature of the single-crystal phosphor sample and the associated fluorescence decay time, the resulting measurements will yield the thermodynamic temperature of the sample over the entire response range of the particular phosphor being used. A thermometer in thermal equilibrium with the sample, eg., a platinum resistance thermometer as suggested in Figure 1, can then be calibrated directly against this new type of primary standard. Realization of the degree kelvin over continuous spans several hundred degrees would then be possible, since some phosphors have very slow variations of decay time with temperature (i.e., they do not quench rapidly).

PROTOTYPE EXPERIMENTAL ARRANGEMENTS

We have carried out a series of experiments aimed at establishing a thermal measurement chain of the type shown in Figure 1. The details of the apparatus are described in several of our early papers on the subject (6,7,8) and in the thesis work of L. J. Dowell (9,10). The original purpose of the studies was to use the system in the “inverse” sense, and calibrate the response of the phosphor thermometer in terms of a NIST-traceable reference thermometry. This was done, and most of the sources of potential experimental uncertainty in such an experimental arrangement were identified (6). One of the principle findings of that work was that one could obtain very pure fluorescence decays from materials such as $Y_2O_3:Eu$, following the initial photo-optical “charging” of the phosphor. See Figure 2 for an example of the measured exponential decay of the fluorescence amplitude. With the availability of samples of single-crystal phosphors suitable for experimental evaluation ($LaPO_4:Eu$ and $Y_2O_3:Eu$), we then carried out sets of studies aimed at demonstrating the feasibility of realizing the degree kelvin with this approach. The initial results with $LaPO_4:Eu$ are described in (8), and those for $Y_2O_3:Eu$ are described in (10). A sample of the temperature-dependent decay times obtained with the $LaPO_4:Eu$ crystals and phosphor is shown in Figure 3. Also shown there are three of the ITS-90 reference points. Using this particular phosphor, continuous measurements (rather than interpolations) between the freezing points of Zn and Al would be possible. A phosphor with a broader thermal roll-off or lower quenching temperature would be needed to reach lower temperatures. An example is $YVO_4:Dy$ phosphor which is also shown in Figure 3.

A simple model based on a publication by Fonger and Struck (11) appears to match the data very well. The equation is

$$\tau = [(1/\tau_0) + b \cdot e^{-(E/kT)}]^{-1}$$

where τ_0 is the the low temperature decay time, b is a ratio of energy transfer rates between energy levels, k is the Boltzmann factor, T is temperature and E is an activation energy. E determines at which temperature quenching begins to occur, b controls the slope of temperature versus decay time. τ_0 is determined by measurement and the curve is produced by adjusting the parameters E and b to match the data.

	\mathcal{G}_0 (s)	E (cm ⁻¹)	b
YVO ₄ :Dy	154	11,800	5.5*10 ¹⁵
LaPO ₄ :Eu	2760	13,500	5*10 ¹³

Optical fibers are used to convey the excitation and fluorescence signal to/from the phosphor under test. This is done because heat leaks associated with clear-air paths into and out of the calibration furnace can then be avoided, thus reducing the size of the thermal gradient in the furnace interior. We mapped the gradient in one candidate furnace used in these studies (Lindberg model 51442), and found that at 1273 EK the maximum measured gradient was < 730 mK mm⁻¹ (12). Details of the analysis algorithms used to extract the exponential decay lifetimes from the raw signals are available elsewhere (13, 14, 15).

PROSPECTS FOR IMPLEMENTATION

The realization of a new primary standard of thermodynamic temperature would be a very ambitious undertaking, and it would ultimately require the resolution of many important metrological issues. The conversion of the temperature measurement into one of obtaining and analyzing a time interval, however, moves the concept in a direction that is generally aligned with modern progress in metrology, since time and frequency are among the most precisely measured of all variables. For instance, Dowell (10) found that by using a Frequency and Time Systems model FTS 4050 cesium beam clock as the time base for his measurements, he was able to achieve a precision in his decay time-based temperature measurements of 0.6% relative to existing thermal standards at temperatures on the order of 1000 EC. He also identified several of the principal components of the error budget in such a measurement. (In fact, the time base was not the limiting factor, but by using the atomic clock for that purpose, the feasibility of making an “absolute” time-based thermal measurement was demonstrated.)

To fully realize the possibilities suggested by this approach, an accurate quantum mechanical model of the temperature dependence of the phosphor’s decay time will be needed. Efforts aimed at developing such models have been reported (16, 17), and further work on this topic is underway. To make such a system readily available to industrial as well as standards laboratories, inexpensive alternatives to laser-based excitation of the phosphor should be used. We have demonstrated that blue LED excitation of rare-earth-doped phosphors is possible (18), thus providing one such alternative excitation source. Lastly, phosphors with a temperature dependent fluorescence decay time that covers as wide a temperature span as possible should be developed and used. We are studying both single-doped (19) and double-doped (20) phosphors that show promise of satisfactory performance. Eventually, long term experiments will be required to establish the durability of the fluorescent material for extended operation at high temperature and over many high/low temperature cycles. In work to be described in more detail elsewhere, an effort has been made to determine the ultimate precision capability in the vicinity of 800 C using the Y₂O₃:Eu phosphor (21,22). A large thermal mass was placed in a high temperature oven so that when the oven’s thermostat was switched off, the temperature decreased rather slowly and approximately linearly in time over the region of interest. The results indicate that a relative drop in temperature of 8.5 mK could be discerned. This matches fairly well investigations by Zhang et al (23) who worked close to ambient temperature with a fiber tipped with a Cr:LiSAF crystal.

In future papers, we hope to describe a fully integrated primary standard based on this approach, and present a comprehensive error budget for it.

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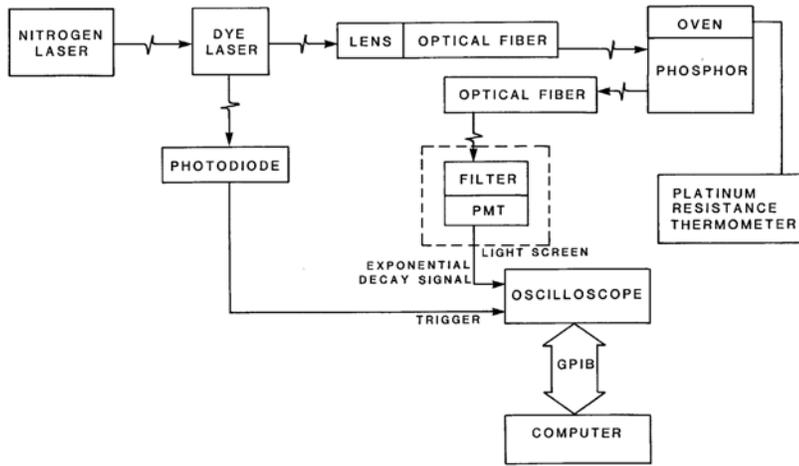


Figure 1. Experimental arrangement for a phosphor thermography measurement system.

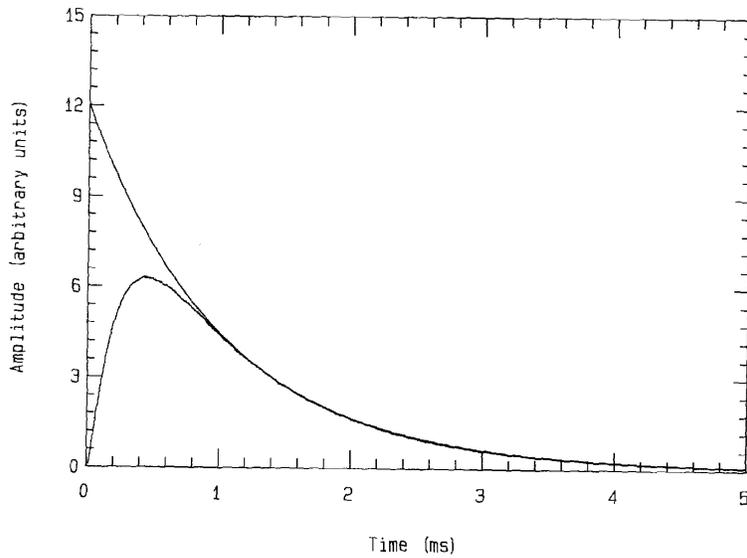


Figure 2. Fluorescence decay of $Y_2O_3:Eu$ (lower curve) vs. a pure exponential (upper curve).

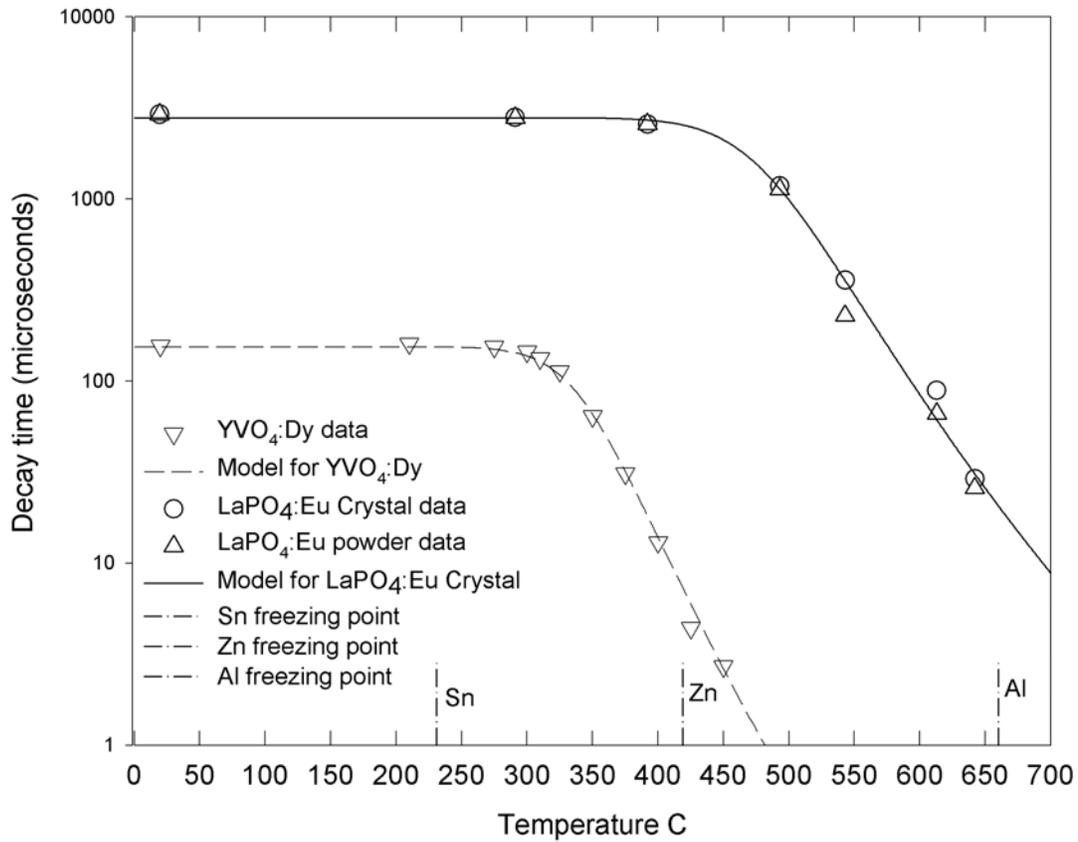


Figure 3. Fluorescence lifetime for LaPO₄:Eu vs. temperature. For comparison, the ITS-90 reference points for Sn, Zn and Al (freezing points) are shown at A, B and C, respectively.