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Topical Review

A brief history of phosphor thermometry

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Abstract

What follows is a brief summary of the history of phosphor thermometry since the first patent submission in 1932 up to the present. There has been an explosion of research and application in the 21st century. A significant body of knowledge and experience has accumulated which is now a resource for future applications.

Keywords: thermometry, phosphors, fluorescence, rare-earths, phosphorescence

(Some figures may appear in colour only in the online journal)

1. Introduction

The luminescence of phosphor materials, whether as powders, paints, coatings, or sputtered thin films, is being used now for a variety of temperature related measurement applications [1–10]. Sometimes the same or similar materials, in the form of an optical fiber, glass or small crystal are also used with the same instrumentation. In recent years the field has branched out from surface thermometry to addressing temperature history with specially developed thermal history paints. Another example involves phosphor particles injected into gas or liquid flows to enable what is now termed thermographic particle image velocimetry (TPIV). Substantial reviews began to appear in the 1990s and continue to the present. A closely allied use with much potential exploits triboluminescence, a property that many phosphors exhibit, for impact and damage sensing [11].

Phosphor materials, when properly excited, emit luminescence. Certain luminescence characteristics can change as a function of temperature. With proper illumination, detection, calibration and test design; temperature determination is accomplished. The basic concept is deceptively simple. However, the execution in practice can be can be very difficult. One reason for this is that most routine and easy temperature measurement situations are readily addressed with relatively inexpensive off-the-shelf sensors, usually thermocouples. Phosphor thermometry is often invoked for very difficult situations where other methods are impossible to implement. It is often the approach of last resort. Such situations demand a customized test design specifically for the circumstances of the particular application. Opportunities to test in the actual environments outside a laboratory may be infrequent and expensive. And such testing is needed in order to elicit problems and subsequently to be able to solve them. The method has been applied to a great number of different situations over the years.

The history of phosphor thermometry in the author's opinion falls into three convenient timeframes.

2. First era 1930–1980

The first known mention of temperature measurement utilizing a phosphor is in two closely related 1937 patents originally filed in 1932 by Paul Neubert [12, 13]. Figure 1 is taken from the earlier one. The patent recognizes the thermal sensitivity of some phosphors. The types of phosphors mentioned are metal sulfides with heavy metals generally. Zinc sulfide with copper was mentioned as a specific example luminous paint. It was cited as particularly suited to the 300 °C to 500 °C range. Interestingly, the temperature to be measured is not the surface to which phosphor is attached/coated. Rather the surface of interest is imaged onto the phosphor coated screen with a lens system. The infrared (IR) emission from the hot surface quenches the phosphor emission. The dimmer regions are hotter. A photograph images the profile.

Franz Urbach began phosphor research in Vienna, Austria in the 1930s at the Institute of Radium Research. He and his wife continued that in the 1940s first at the University of

Rochester and then Eastman Kodak where he headed up their phosphor department. He applied for a patent in 1949 and it was issued in 1951 [14]. He presented the method at an Optical Society Meeting. Here is a quotation from a local newspaper by a reporter who attended [15] 'Used as a paint on a kettle, engine, radio tube or the side of your house, the phosphor shows all the different temperatures by yellow colors. …The paint shows heat changes that never could be seen before, the warming-up of a radio tube and the boiling of a still'.

Figure 2 is taken from that patent and shows the relative brightness of several materials for use in different temperature ranges. In the figure, the phosphors are designated by a number. The list below is a key for identifying those phosphors. 62 and 69 would go on to be the most important ones in subsequent work.

Number	Phosphor	Temperature range °C
60	Sr_2WO_5	−200 to 100
61	$ZnMoO_4$	−100 to 0
62	ZnSCdS(Ag,Ni)	−50 to 50
63	$Na_2W_2O_7$	0 to 100
64	$ZnWO_4$	50 to 125
65	Same as 62 but greater illumination	−50 to 175
66	$CdWO_4$	100 to 150
67	$CO_2B_2O_5$(Mn)	25 to 200
68	$MgWO_4$	100 to 200
69	ZnS:Ag,Cu	225 to 400
70	Same as 67 lower illumination	0 to −200

It may be noticed that rare earth phosphors are missing. Eventually rare-earth phosphors will be developed for many display, lighting and scintillation applications and will be put into service for phosphor thermometry.

It should be emphasized that the method was based on the brightness of the luminescence. For each application, the brightness versus temperature curve must be measured under identical conditions as the application. For instance, if the light source dims or distances change, the curve is invalid. One of the first applications of this new method was to aerodynamics. An example was a measurement of flow past a flat plate with a knife edge by Bradley [16]. That work further informs that US Radium obtained the patent rights from Eastman Kodak and marketed the technique, developing new phosphors, the Radelin product line, and a lacquer for attaching to surfaces. This is described in US Radium data sheet 40.40 titled 'Thermographic Phosphors and Contact Thermography'. This brochure may be found in the Appendix of a report on reliability and accelerated stress factors on solar cells. The authors used the technique in the course of their work [17]. In this data sheet, US Radium acknowledges Urbach and that they have developed improved phosphors. Their term for the method is Contact Thermometry. They recommend that it is good for 'measure of variation of temperature', an effective monitor in two dimensions and, interestingly, 'variable electrical conductivity of thin surface layers'. They say it is especially good for showing flaws in bonding of laminates for instance. They note that short wavelength infrared light impinging on the phosphor will affect the brightness and hence the perceived temperature profile. They give practical advice on light sources with list of vendors. There is a section on coating methodology. For room temperature, normally the first try should be Radelin 1807 which is ZnCdS:Ag,Ni. The Ni is a judiciously added poison to the luminescence. It could be brushed onto a surface for qualitative work, but normally the optimum thickness is 5 mil or about 125 microns. They suggest an air brush to use.

Other significant work beginning in the 1950s occurred in France [18, 19]. Thureau may have been the first to discuss the temperature dependence of spectral distribution and the approach of taking the ratio of different spectral bands. Figure 3 is directly from [19] and used by permission of the Directorate General of Armaments—Technical and Economic Intelligence (DGA-ITE) of France. Clearly, the shorter wavelengths exhibit stark temperature dependence whereas above 590 nm there is slight or no such response. Charwat [20] describes using Thureau's approach for wind tunnel tests. It is clear Thureau's work was known and being used in the US. The ratio technique to our knowledge was the only approach for applications outside the laboratory until the 1980s. His doctoral thesis [18] is an impressive work especially considering the limited laboratory tools available then. Benoit Fond, who assisted the author in obtaining this document discovered that he seeded luminescent particles into gases for flow measurement. This idea would not be pursued further until the 21st century. Fond, the co-author of a review of the thermographic particle velocimetry approach [9], and the present author are both impressed by this and glad to make it known. Thureau was followed by Leroux who was the first, to our knowledge, to exploit the change in temporal character of the emission with temperature. Using periodic excitation, the temperature dependence of the phase shift was exploited as well as the modulation depth. Rise and decay time temperature dependence was also noted [21].

The Midwest Research Institute of Kansas City, Mo performed some early research on thermographic phosphors [22,23] Gross *et al* discussed the mechanisms of temperature dependence and derived some basic relations. One is termed CT, which is 'the temperature coefficient of relative luminosity'. And, it is the change in luminosity per degree divided by mean luminosity of temperature increment. The aim was to find how to design phosphors to maximize temperature sensitivity. Another activity in this report concerned measuring temperature sensitivity and calibration. They claimed it is too slow and tedious to use a photocell to monitor temperature as an illuminated target gradually warms from a very low to a high temperature. They indicated one could not trust the light source to remain constant in intensity over the many hours required. So, they developed the controlled temperature gradient device. At one end the specimen is hot, the other cold. The specimen's emission is sent through a prism and imaged onto a camera. The resulting photograph yields brightness versus temperature at the dispersed wavelengths, a clever design.

An influential 1961 paper by Byler and Hayes of US Radium described the use of their Radelin product line of thermographic phosphors for temperature measurement [24]. An example of practical application and sustained use of those

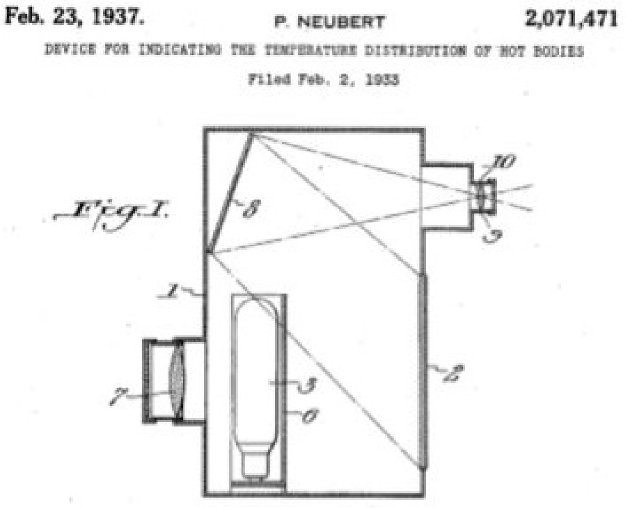

Figure 1. Illustration from Neubert patent (12).

phosphors is described by Cysz and Dixon at AEDC (Arnold Engineering Development Center). Their aerospace application utilized what they termed ‘impulse wind tunnels’ for heat flux distributions [25, 26]. The aerodynamic test models were first coated with epoxy. Then a mixture of phosphor and acetate lacquer would be applied on top. They achieved millisecond time response and temperature resolution of ~0.7 C and heat flux resolutions of about 0.1 watts m^{-2}. The measurement was accomplished using an isodensitometer to map the optical density of photographic negatives. They calibrated optical density to temperature with strategically located discrete thermocouples. They indicate encountering visible and infrared background radiation due to what they call the ‘gas cap on blunt bodies’. They stated it was readily filtered so as not to interfere with the yellowish phosphor emission that indicates temperature. The presence of background emission such as this can still be an impediment for modern pyrometers. One example of their testing involved a scale model of a Gemini space capsule [25, 26].[1] To aid the reader in visualizing such a model, figure 4 is an artist’s depiction from when the Gemini program was first announced by NASA. The scale model was placed in the wind tunnel such that the nose seen on the right side in the image faces the wind.

A temperature measurement of the surface of an electronic component is described by Fry of Bell Labs [27]. It is an excellent example, well described, of the painstaking attention to detail necessary to make such measurements. The surface of interest was a transistor chip in an integrated circuit voltage regulator. He used Radelin #3251 which is ZnCdS:Cu, Ni, or Ag. He mapped temperature on a 1 mm square area with a spatial resolution of 40 μm square, the size of the microdensitometer aperture.

A uniform phosphor coating was applied to 24 karat 5 mm square, 0.5 mm thick gold squares for reference and calibration. Cu chips had to be rejected because of reaction with the ZnS. The size of the particles in the phosphor sample involved too wide of a range so a particle analyser was used to sift down to a particle range between 6 to 10 microns. The fiber optic photometer, the major component of the microdensitometer, was calibrated with a US National Bureau of Standards (NBS) traceable standard. (Note that the NBS is now the National Institute of Science and Technology—NIST). An 85 °C to 95 °C gradient across the 1 mm square was measured. A similar effort by Brenner addressed transistor temperatures is also instructive for its clear description of the procedure and attention to detail [28].

The growth and dissemination of the method from its inception to the intoduction of the first commercial product was slow. Data acquisition and analysis with the tools of the time was laborious and tedious. Perhaps the most extensive use was for aerodynamic heating studies in wind tunnels. Finally, near the end of this era, many optical laboratory components now common became commercially available such as optical fibers, ultraviolet lasers, and high quality silica lenses. This, plus improvements to electronics enabled the next stage of phosphor thermometry development.

What signifies the end of this first era is the appearance in 1979 of the first phosphor-based commercial thermometer by Luxtron. For this, phosphor was attached to the end of an optical fiber and deployed where desired such as inside power line transformer coils or a microwave oven. The other end of the fiber connected to a compact benchtop package containing an ultraviolet light source and associated optics and electronics. Figure 5 is a photograph from Luxtron product literature.[2] It used a rare-earth Eu^{3+} phosphor and determined temperature from the ratio of two bands, achieving temperature resolution of 0.1 °C. Also important was a widely read seminal article by Wickersheim and Alves, both of Luxtron, on recent advances in optical thermometry where they described the method [29] as well as other optical approaches. It was where this author learned about the technique. Luxtron is now Advanced Energy and continues to manufacture phosphor thermometry products.

3. Second era 1980–2000

Research and development in the period of 1980 to 2000 was directed to a variety of situations. The following list summarizes the new tools and methods applied to phosphor thermometry in this period.

- Lasers and LEDs as light sources
- The decay time approach
- Distant and moving surfaces
- Fiber Optics
- Durable coatings (E-beam, RF sputtering, plasma spray etc)
- Rare-earth and other types of phosphors utilized
- Temperatures ≫ 400 °C

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[1] Project Gemini was NASA’s second manned spaceflight program. The Gemini capsule carried two people. The program lasted from 1961 to 1966 and set the stage for the Apollo program and the landings on the moon (www.nasa.gov/image-feature/from-mercury-mark-ii-to-project-gemini).

[2] Product brochure titled ‘Fluoroptic Thermometry’ dated Feb 1982 by Luxtron Inc. Luxtron is now part of the Advanced Energy (www.advancedenergy.com).

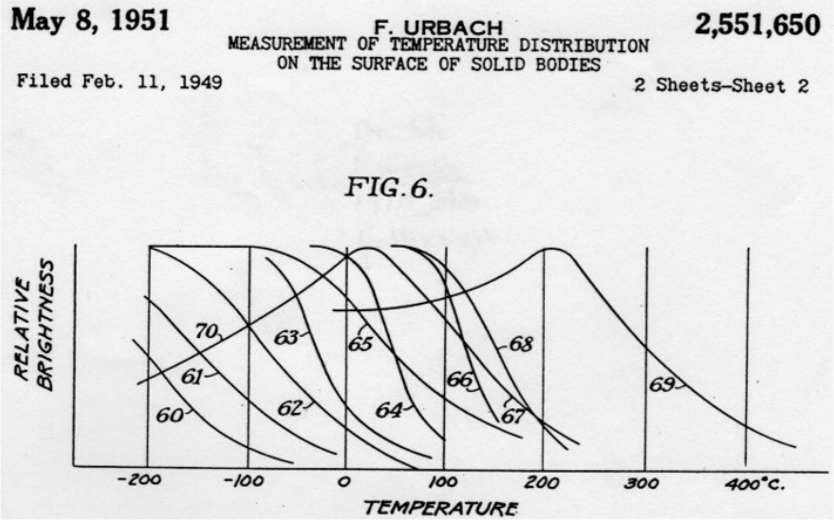

Figure 2. Figure 6 of Urbach patent (14).

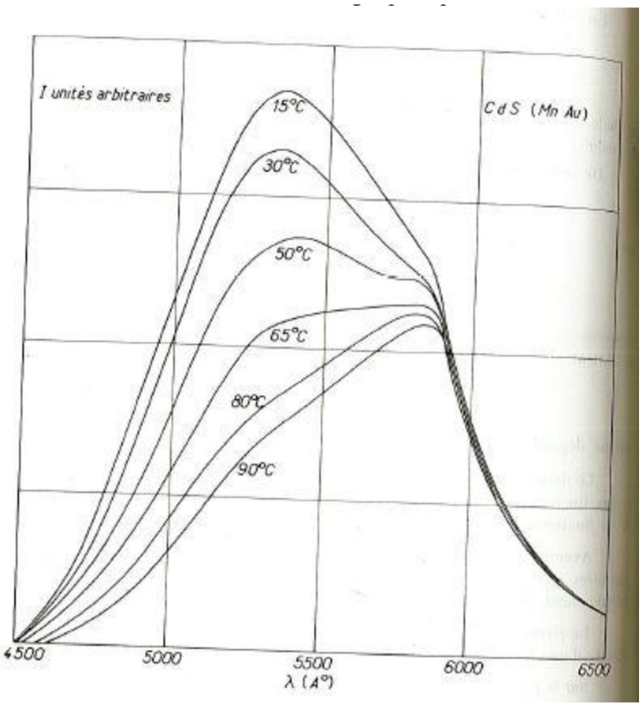

Figure 3. Spectral Distribution from 15 °C to 90 °C for a specific phosphor, from Thureau. Reproduced with permission from the DGA-ITE [19].

By 1980, Q-switched Nd:YAG and N_2 discharge lasers were commercially available. They emitted high energy in short bursts of a few nanoseconds. The observation and measurement of phosphor decays was therefore easier to accomplish than before. Early on red LEDs were investigated as light sources for Cr-doped materials. Eventually, LED output became more efficient, brighter and moved even into the ultraviolet where more phosphors could be excited. They became a viable excitation source for some applications by the end of this period.

Another result of the use of high power lasers was that phosphor-coated targets could be illuminated and detected from greater distances than before. In addition, measuring surface temperatures of moving targets such as high speed speed motor armatures and turbine blades was now feasible.

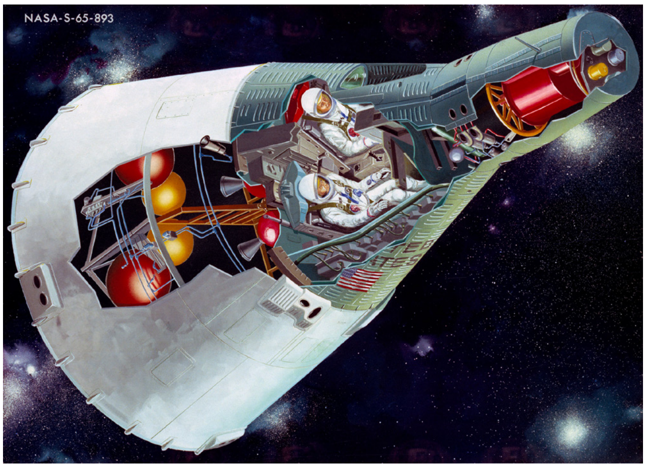

Figure 4. Artist Rendition of Project Gemini Space Capsule. Image Credit: NASA.[1] Courtesy of NASA [27].

Also, by 1980 silica optical fiber was available which could transmit near ultraviolet laser light efficiently for several meters. And the transmission properties continued to improve. It is much easier to couple light into optical fiber from a laser than from extended sources such as ultraviolet lamps. So the use of optical fiber in the research and development of the method for different applications proliferated. This made it possible to perform measurements of remote locations such as inside jet turbine and automobile engines.

For deployment in high temperature and erosive environments such as in engines, durable coating methods are required. Thus electron-beam deposition, RF-sputtering, plasma spray methods were investigated and adequately demonstrated.

Prior to 1980, the temperature limit for phosphor thermometry, as far as can be determined from available literature, was 400 °C. With high power light sources and new phosphors, the limit was extended to 1200 °C. Many new phosphors were characterized during this period, typically activated with rare-earth or transition metal dopants. An advantage was that none of them involved carcenogenic Cd, the constituent of some of the Radelin phosphors used in earlier decades.

Figure 5. Initial Luxtron Phosphor-Based Thermometry System. Reproduced with permission from Advanced Energy [30].[2]

4. Third era 2000-present

In the 21st century efforts throughout the world are expanding. A good number of universities have programs of long duration and are making many contributions. Also, temperature measurement on the micro and nanoscales is receiving a great amount of attention [8], often with biological and biomedical motivations. During this period, the number of people involved in research and development has increased dramatically. A great number of new thermographic materials are being custom-designed and explored. This is in contrast to earlier times when most investigations utilized phosphor materials originally developed for lighting or scintillating applications simply because they were available. Applications involving imaging hardware are proliferating and producing valuable results.

During this period the field has branched to other similar allied areas:

- Rare earth-doped thermal barrier coatings for temperature, wear, coatings health etc [30]
- Thermal History Paints [7]
- Thermographic particle image velocimetry (TP-PIV) [9]
- Triboluminescence [11]

A significant body of knowledge and experience has accumulated which is now a resource for future applications. The depth and breadth of research and development merited the conference and proceedings in this issue of Measurement Science and Technology.

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