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# Influence of codoping on the luminescence properties of YAG:Dy for high temperature phosphor thermometry

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ABSTRACT

The effects of codoping on the temperature-dependent luminescence of YAG:Dy were investigated for application in high temperature thermometry. YAG:Dy is a well-known thermographic phosphor suitable for high temperature measurements. However, its decay time is too long for studying temperatures in fast transient technical processes. Codoping is a known method for increasing the signal intensity and for decreasing luminescence decay times. Five co-doped samples with three different sensitizers, namely Tm, Tb and Pr were synthesized by solid-state method. Changes in spectral emission behavior and temperature dependent decay time are presented up to 1600 K. The intensity ratio used for temperature measurements was similar for all samples, and decay time decreased for all codopings. Codoping by Tm decreased signal intensity considerably, thus YAG:Dy,Tm is not suitable for high temperature measurements. However, codoping YAG:Dy with Tb and especially Pr resulted in improved luminescent characteristics, and these phosphors are promising for high temperature phosphor thermometry.



## 1. Introduction

Thermographic phosphor thermometry has become an established technique for remote and non-intrusive temperature measurements. The phosphors employed usually consist of a ceramic powder host matrix doped with a rare-earth or transition metal activator. They are means to provide temporally and spatially resolved temperature fields for both surface temperature measurements [1] as well as for thermometry of gaseous flows [2–4].

Depending on the technical application studied, phosphors with different characteristics such as temperature sensitivity range, decay time, luminescence intensity, emission wavelength or cross sensitivities are needed. Investigation of the thermographic properties for various phosphors were presented by Allison and Gillies [4] and Aldén et al. [5]. An overview over the decay time characteristics of different phosphor materials is given in [1]. An extensive summary on phosphor applications for different temperature ranges can be found in [6,7]. The phosphorescent materials mainly used for high temperature thermometry are presented in Table 1. The widest temperature range is covered by YAG:Dy and YAG:Tm showing temperature dependent exposure times of $1–10^3$ μs or $0.1–10^2$ μs, respectively.

The luminescence properties of thermographic phosphors strongly depend on the interaction between host lattice and dopant ions. As a rule, rare earth activators have a weak coupling of the 4f electrons with the lattice. This results in narrow emission lines and higher thermal quenching temperatures, which is advantageous in comparison to transition metals [22]. The YAG crystal structure is body-centered cubic, with the rare earth dopant substituting $^3$Y at the dodecahedral $^3$Y-sites in the crystal lattice [23].

In general, increasing temperature influences the spectral behavior of rare earths. Thermalization effects occur when two energy levels lie relatively close together, as for example the $^4F_{9/2}$ and the $^4I_{15/2}$ energy levels of YAG:Dy. At higher temperatures the population of higher energy levels rises, changing the intensity distribution of the spectrum corresponding to Boltzmann's law. The radiative transition decay time is reduced due to quenching, vibrational relaxation and internal conversions. Additionally, broadening of linewidth becomes more pronounced caused by lattice vibrations [24].

The Dieke diagram can help to understand the emission behavior of the activator ions. An excerpt for the four studied rare earths, namely $Dy^{3+}$, $Pr^{3+}$, $Tm^{3+}$ and $Tb^{3+}$ is given in Fig. 1.

$Y_3Al_5O_{12}$ (YAG) has proven to be an efficient host for high

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**Table 1**
Survey of main phosphors employed for high temperature measurements.

| Phosphor | Temperature range | Decay time | References |
|---|---|---|---|
| YAG:Dy | 300–1700 K | $1 \times 10^3$–1 μs | [8–11] |
| YAG:Pr | 300–1100 K | 190 μs | [12–14] |
| YAG:Tm | 300–1700 K | $1 \times 10^2$–0.1 μs | [15,16] |
| $Y_2O_3$:Eu | 290–1300 K | $1 \times 10^3$–1 μs | [17,18] |
| $GdAlO_3$(GAP):Cr | 300–1350 K | $1 \times 10^4$–1 μs | [19] |
| $BaMg_2Al_{10}O_{17}$(BAM):Eu | 300–1300 K | 2–0.01 μs | [20,21] |

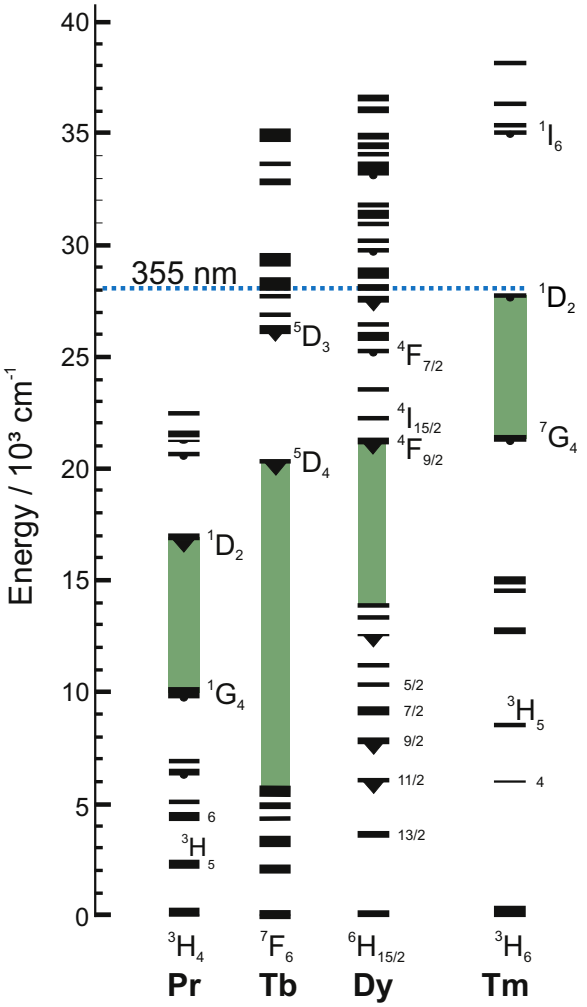


**Fig. 1.** The Dieke energy diagram for the rare earths $Pr^{3+}$, $Tb^{3+}$, $Dy^{3+}$ and $Tm^{3+}$ following [25]. The green shading between levels notes the largest energy gap for the rare earths. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

temperature thermometry, having a high melting point of 2213 K [26]. Moreover, many lanthanide activators show higher temperature sensitivity ranges in YAG as in other host matrices [1]. YAG:Dy is widely used in combustion application for thermometry showing emission up to 1700 °C from both $^4F_{9/2}$ and $^4F_{7/2}$ level [16,27], see Fig. 1. Its emission characteristics are not affected by combustion environments [28]. YAG:Dy has the additional advantage of emitting in the blue region, thus being less affected by black body radiation at high temperatures [21]. Based on the work of Heyes [22], who developed a method to design phosphors for high temperature, at the moment YAG:Dy is the phosphor with the highest capability for thermometry at high temperatures.

However, YAG:Dy has a long emission decay time of several 100 μs at room temperature. This introduces measuring inaccuracies at short exposure times of the detector due to low signals. At long exposure times black body radiation at high temperatures cannot be satisfactorily suppressed [21].

In addition, high-temperature thermometry above 1000 K is still limited because of signal loss due to thermal quenching. It is possible to simultaneously reduce quenching and improve luminescence intensity by substituting the tetrahedral site $Al^{3+}$-$O^{2-}$ in YAG:Dy with $B^{3+}$-$N^{3-}$ [29,30]. Enhanced $Dy^{3+}$ emission by a factor of 2.5–4 has been observed for $Gd_3Al_5O_{12}$ stabilized with $Lu^{3+}$ compared to the simple YAG:Dy [31].

Another option to improve luminescence properties is to use a second sensitizer in addition to the original activator. Codoping YAG:Dy with $Er^{3+}$ [8,27] or $Bi^{3+}$ [32] led to an increase in signal intensity, the latter enhancing luminescence by about seven times at room temperature. Enhanced luminescence has also been observed for codoping $Y_2Zr_2O_7$:$Dy^{3+}$ with $Li^+$ [33].

Using alternative codoping combinations can also increase luminescence intensity while decreasing the decay time simultaneously. Of special interest for high temperature applications are other rare earth sensitizer such as $Tm^{3+}$, $Tb^{3+}$ and $Pr^{3+}$. These lanthanide ions have similar excitation wavelengths, are temperature sensitive and both $Tm^{3+}$, and $Pr^{3+}$ have shorter decay times than $Dy^{3+}$ [12,15].

Energy transfer processes between $Dy^{3+}$ and $Tb^{3+}$ were studied in a $YF_3$ matrix [34], for gadolinium oxide hosts [35] and $Y_2O_3$ nanophosphors [36]. Likewise the effect of codoping $Dy^{3+}$ ions with $Tb^{3+}$ ions has been studied for various glasses [37–40], finding non-radiative energy resonance transfers due to dipole-dipole interactions. In this context shorter decay times of about 25% of the original time for the $Dy^{3+}$ luminescence were presented [34,37]. Temperature dependence from 30 K to 300 K as well as decreasing decay times with higher Tb concentrations in $Dy^{3+}$-$Tb^{3+}$ codopings have been observed for a $CaMoO_4$ host matrix [41].

Energy transfer between $Tm^{3+}$ to $Dy^{3+}$ has been observed for tellurite [42] and selenide [43] glasses. YSZ co-doped by ($Dy^{3+}$ + $Tm^{3+}$) was used for studying luminescence intensity of thermal barrier coatings, focusing on porosity and phase composition [44].

No information on codoping effects for $Dy^{3+}$ and $Pr^{3+}$ ions can be found in the literature. However, singly-doped YAG:Pr has a short luminescent lifetime while offering good temperature measurement capabilities up to 1100 K [12].

This paper concentrates on the influence of $Tm^{3+}$, $Tb^{3+}$ and $Pr^{3+}$ codopings on the luminescent behavior of YAG:Dy. Different activator concentrations are presented and their influence on the absolute signal intensity, the decay time and the spectral behavior are studied.

## 2. Materials and method

### 2.1. Sample preparation and characterization

$Y_{(3-x)}Al_5O_{12}$:x% $Dy^{3+}$ and $Y_{(3-x-y)}Al_5O_{12}$:x % $Dy^{3+}$, y% $RE^{3+}$ phosphors were fabricated by conventional high temperature solid-state method, with RE being $Pr^{3+}$, $Tb^{3+}$ and $Tm^{3+}$ respectively. In the following sections the expression of $Y_{(3-x)}Al_5O_{12}$:x% $Dy^{3+}$ and $Y_{(3-x-y)}Al_5O_{12}$:x % $Dy^{3+}$, y% $RE^{3+}$ are abbreviated as YAG:Dy(x%),RE(y%), where x is the dopant concentration in mol % and y is the sensitizer concentration in mol %, respectively. In order to decrease sintering temperature and to improve the phosphor efficiency $B_2O_3$ was chosen as a flux. Stoichiometric amounts of $Y_2O_3$,$Al_2O_3$, $Pr_2O_3$, $Tb_2O_3$, $Tm_2O_3$, $B_2O_3$ (all, 99.99%, Alfa Aesar) $Dy_2O_3$ (99.9%, Reacton) were used as starting materials in the present work. The starting powders were mixed and ground in an agate mortar by hand. Subsequently, they were fired in an alumina