Inorganic Phosphors for Temperature Sensing in Hydrogen-Rich Environment

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Abstract:

Inorganic phosphor materials can be used for temperature measurements since the lifetime of phosphorescence is temperature dependent. For practical applications, the lifetime in the range of milliseconds to microseconds is required and this condition limits the choice of activators to ${\rm Cr}^{3^+}$ and ${\rm Mn}^{4^+}$ among the 3d metals. The working environment and instrumental features puts additional constraints on the chemical and temperature stability, absorption and emission profiles of phosphors. This paper discusses development of phosphor materials for operation in the hydrogen-rich environments, such as Canadian oil fields. Presence of hydrocarbons leads to saturation of optic fibers with hydrogen and attenuation of light above 705 nm, the emission wavelength of the ${\rm Cr}^{3^+}$ -doped ${\rm Y_3Al_5O_{12}}$ temperature phosphor. Using chemical tools, a phosphor with longer emission wavelength was developed. This phosphor also meets the other requirements imposed by the current instrumentation.

Key words: temperature sensors, inorganic phosphors, emission, lifetime.

Background and requirements

Intensity and decay time of the light emitted by a phosphor are temperature dependent and can be used for temperature measurements. In one approach, the intensity ratio for two emission lines is used; in the other, the decay rate of the intensity of one emission line is utilized. The latter method is technologically simpler and is incorporated into the fiber optic temperature sensors developed by Photon Control Inc. Intensity, I, of the emitted light decreases exponentially with time, t, $I = I_0 \exp\left(-\frac{t}{\tau}\right)$,

with I_0 being the initial intensity and τ the decay time (or lifetime). Typically, the decay time is temperature dependent and decreases linearly (on the log scale) with temperature. In a fiberoptic sensor, a phosphor is excited with a laser pulse and the decay time is determined by monitoring the intensity of the emitted light. For phosphor materials, the decay time of 10^{-6} - 10^{-3} s is preferred as it can be precisely and inexpensively measured.

The ${\rm Cr}^{3^+}$ (3 ${\it d}^3$) cation is extensively used in the phosphor materials due to its high efficiency, long lifetime, suitable absorption and emission wavelengths. The Photon Control Inc. uses the Cr-doped ${\rm Y}_3{\rm Al}_5{\rm O}_{12}$ garnet for temperature

detection in the non-hydrogen rich environments. However, this material cannot be employed when hydrogen is present.

For operation in the hydrogen-rich environment and to be compatible with the current instrumentation, a new phosphor should be (1) chemically inert, have (2) photoluminescent (PL) emission in the 750-850 nm range, (3) excitation between 530 and 700 nm, and (4) decay time of milliseconds at room temperature.

Approach

The molecular states for Cr³+ in an octahedral crystal field as well as the effect of the crystal field strength on their energy are presented in the Tagano-Sunabe diagram (Fig. 1). The PL emission in Cr³+ originates from the transition from the ²E state to the ⁴A₂ one. To shift the emission to a longer wavelength (lower energy) one must decrease the energy separation between these two states. As the slope of the ²E curve is small, the effect of the crystal field on the emission energy will also be small. To tune the PL wavelength, a significant weakening of the crystal field is required. This is

achieved by introducing large atoms into the host structure.

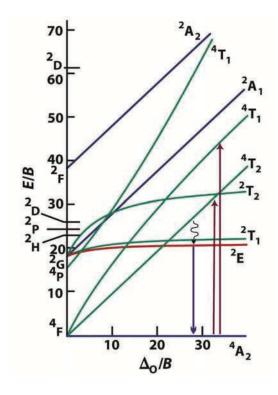


Fig. 1. Molecular states for Cr^{3+} in an octahedral field. The $^2E \rightarrow ^4A_2$ transition yields PL.

Results

The reduction in the crystal field and shift of the emission wavelength was achieved by introducing larger atoms into the host structure of $Y_3Al_5O_{12}$. Fig. 2 shows the absorption and emission profiles of the Cr^{3+} -doped $Y_3Al_5O_{12}$ while Fig. 3 the same for the targeted phosphor material.

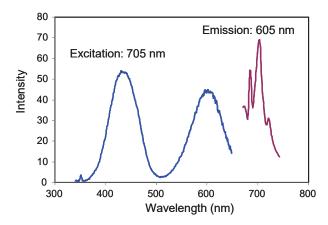


Fig. 2. Excitation and emission profiles of Cr^{3+} -doped $Y_3Al_5O_{12}$.

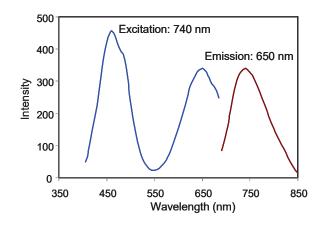


Fig. 3. Excitation and emission profiles of Cr³⁺-doped targeted phosphor.

The new phosphor has a lifetime of 0.103 ms at room temperature. While its lifetime and emission intensity decreased, they are still within required operational parameters. On the other hand, chemical stability and absorption fully meet the target values.