

Temperature Sensing Above 1000°C Using Cr-Doped GdAlO₃ Spin-Allowed Broadband Luminescence

Jeffrey I. Eldridge^a and Matthew D. Chambers^b

^aNASA Glenn Research Center, Cleveland, OH 44135, USA

^bRaytheon Vision Systems, Goleta, CA 93117, USA

Abstract. Cr-doped GdAlO₃ (Cr:GdAlO₃) is shown to produce remarkably high-intensity spin-allowed broadband luminescence with sufficiently long decay times to make effective luminescence-decay-time based temperature measurements above 1000°C. This phosphor is therefore an attractive alternative to the much lower luminescence intensity rare-earth-doped thermographic phosphors that are typically utilized at these elevated temperatures. In particular, Cr:GdAlO₃ will be preferred over rare-earth-doped phosphors, such as Dy:YAG, at temperatures up to 1200°C for intensity-starved situations when the much lower emission intensity from rare-earth-doped phosphors is insufficient for accurate temperature measurements in the presence of significant radiation background. While transition-metal-doped phosphors such as Cr:Al₂O₃ (ruby) are known to exhibit high luminescence intensity at low dopant concentrations, quenching due to nonradiative decay pathways competing with the ²E to ⁴A₂ radiative transition (R line) has typically restricted their use for temperature sensing to below 600°C. Thermal quenching of the broadband ⁴T₂ to ⁴A₂ radiative transition from Cr:GdAlO₃, however, is delayed until much higher temperatures (above 1000°C). This spin-allowed broadband emission persists to high temperatures because the lower-lying ²E energy level acts as a reservoir to thermally populate the higher shorter-lived ⁴T₂ energy level and because the activation energy for nonradiative crossover relaxation from the ⁴T₂ level to the ⁴A₂ ground state is high. The strong crystal field associated with the tight bonding of the AlO₆ octahedra in the GdAlO₃ perovskite structure is responsible for this behavior.

Keywords: Luminescence, phosphor, temperature measurement

INTRODUCTION

Optical temperature measurements using luminescence decay of thermographic phosphors is a well-established technique, and a variety of phosphors with different ranges of temperature sensitivity have been demonstrated that, in combination, cover the temperature range from absolute zero to 1700°C.¹⁻⁴ For making temperature measurements above 1000°C, thermographic phosphors incorporating rare-earth dopants, such as Dy³⁺, Tm³⁺, Tb³⁺ and Eu³⁺, have been utilized almost exclusively. The 4f electrons in these rare-earth dopants are shielded by the 5s and 5p electrons, resulting in weakly phonon-coupled, spin-forbidden 4f electron transitions. This weak phonon-coupling delays thermal quenching to much higher temperatures compared to transition metal dopants with unshielded 3d electrons. Unfortunately, the oscillator strengths for the 4f transitions are several orders of magnitude weaker than for the 3d transitions,⁵ resulting in much lower luminescence emission intensity. This low luminescence emission intensity produced by rare-earth dopants, especially in the presence of the intense background thermal radiation that is common in industrial applications, has been a severe impediment for the successful

implementation of thermographic phosphors at temperatures above 1000°C. The more attractive high luminescence intensity observed from transition-metal-doped phosphors has not been previously achievable for temperature measurements above 1000°C because strong phonon coupling produces thermal quenching at lower temperatures; for example, temperature measurements using the decay of the luminescence from Cr:Al₂O₃ (ruby) have an upper temperature limit of about 600°C.⁶⁻¹³ A secondary drawback to utilizing Cr³⁺ dopant luminescence is that emission occurs at long wavelengths (~700 nm R-line emission) where the background thermal radiation is much more intense than at the shorter emission wavelengths produced by rare earth dopants selected for high temperature measurements (e.g., 456 nm emission from Dy:YAG).^{1,2,14-16}

This paper presents a novel use of the spin-allowed broadband luminescence emission from Cr-doped GdAlO₃ (Cr:GdAlO₃)¹⁷ that offers the benefit of high luminescence emission intensity typical of a transition metal dopant, but with thermal quenching delayed to the much higher temperatures normally associated with rare-earth dopant luminescence. In addition, the spin-allowed broadband emission extends the range of useful Cr³⁺ luminescence towards shorter wavelengths (<600 nm) where thermal background

radiation is less intense. The Cr:GdAlO₃ thermographic phosphor (and closely related phosphors)¹⁷ therefore offers superior performance to rare-earth-doped thermographic phosphors to at least 1200°C in any situation where the much weaker rare-earth dopant luminescence limits temperature measurement accuracy and reliability.

Rationale for Selection of Cr:GdAlO₃

Transition metal dopants are not usually considered for thermographic-phosphor-based temperature measurements above 1000°C due to the aforementioned thermal quenching at lower temperatures. Furthermore, spin-allowed broadband luminescence emission from transition metal dopants typically exhibits much shorter radiative decay times and stronger thermal quenching than the spin-forbidden R-line emission. However, Zhang et al.⁷ have shown that in high-crystal-field Cr³⁺-doped crystals, the long-lived ²E energy level can act as a reservoir for the higher lying ⁴T₂ energy level that is responsible for the spin-allowed broadband emission via radiative relaxation to the ⁴A₂ ground state. Fig. 1 shows a single configurational coordinate plot for high-crystal-field (where the ⁴T₂ level is higher in energy than the ²E level) Cr³⁺-doped crystals (such as Cr:Al₂O₃ and Cr:GdAlO₃), where ΔE is the energy difference between the ⁴T₂ and underlying ²E levels, ΔE_q is the energy barrier between the zero-phonon ⁴T₂ state to the ⁴T₂-to-⁴A₂ crossover by multiphonon absorption, and Δ_{FC} is the Franck-Condon offset between the ⁴T₂ and ⁴A₂ parabolas. At increasing temperatures, thermal equilibrium between the ²E and ⁴T₂ levels results in an increasing promotion of ions from the much longer-lived ²E reservoir level to the ⁴T₂ level. Therefore, the spin-allowed broadband radiative relaxation from the ⁴T₂ to ⁴A₂ ground state increases as the emission associated with the spin-forbidden ²E to ⁴A₂ radiative transition decreases. At even higher temperatures, non-radiative crossover from the ⁴T₂ to ⁴A₂ states increases due to higher phonon population levels and leads to the eventual thermal quenching of the spin-allowed broadband emission. Because thermal equilibrium is maintained between the ²E and ⁴T₂ populations, the observed decay time of the observed ²E to ⁴A₂ emission, τ_{2E}, and that of the ⁴T₂ to ⁴A₂ broadband emission, τ_{4T2}, both reflect the depopulation of the ²E reservoir. Therefore, τ_{2E} = τ_{4T2}. Zhang et al.⁷ showed that the decay time associated with these ²E reservoir depopulation processes as a function of temperature, T, can be expressed by:

$$\tau_{4T2} = \tau_{2E} = \tau_{2E}^R \frac{1 + 3e^{-\Delta E/kT}}{1 + \alpha e^{-\Delta E/kT} + \beta e^{-(\Delta E_q + \Delta E)/kT}} \quad (1)$$

where 1/τ_{2E}^R is the intrinsic radiative rate of the ²E to ⁴A₂ transition, α = τ_{2E}^R/τ_{4T2}^R, β = τ_{2E}^R/τ_q, 1/τ_q^R is the intrinsic radiative rate of the ⁴T₂ to ⁴A₂ transition, 1/τ_q is a scaling factor for the nonradiative ⁴T₂ to ⁴A₂ crossover rate, and k is Boltzmann's constant. Assuming α and β ≫ 1, this relationship shows that thermal quenching of the observed broadband ⁴T₂ to ⁴A₂ transition can be delayed to higher temperatures by increases in ΔE and in ΔE_q. Tanabe-Sugano diagrams for 3d³ electron configurations indicate that ΔE increases with the strength of the crystal field.^{7,18} Furthermore, ΔE_q becomes greater for stronger bonding, since the stronger restoring force on a displaced ion will result in a greater steepening of the ⁴T₂ parabola (which involves bonding orbitals) than the ⁴A₂ parabola (which does not involve bonding orbitals).

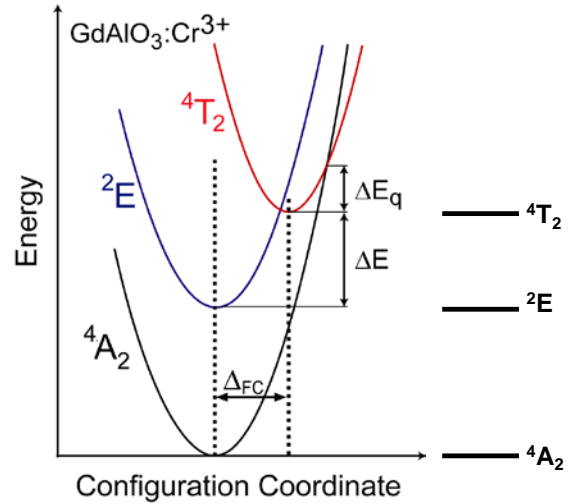


Figure 1. Single configurational coordinate plot (left) and energy level diagram (right) for high-crystal-field Cr³⁺-doped phosphors such as Cr:GdAlO₃.

In view of these considerations, rare-earth aluminate orthorhombic perovskites, REAlO₃, are ideal crystal hosts for Cr³⁺ dopants. The Cr³⁺ dopant ions substitute for the Al³⁺ ions in the tightly bound AlO₆ octahedra within the REAlO₃ perovskite structure,¹⁹ resulting in exceptionally strong crystal fields (20% higher at Al³⁺ sites in GdAlO₃ compared to Al₂O₃).²⁰ Among the rare-earth aluminate perovskites, REAlO₃, only the perovskites with RE = Gd, Tb, Dy, Y, Ho, Er, and Tm retain an orthorhombic perovskite structure from room temperature to above 1000°C.²¹ The others exist in either rhombohedral or cubic structures,²¹ with undistorted cubic symmetry at the Al³⁺ sites in the AlO₆ octahedra, and therefore will exhibit undesirably weak excitation transition oscillator strengths. Among

the remaining candidate rare-earths, the crystal field at the Al^{3+} octahedral sites is expected to decrease in the order from largest to smallest ionic radii ($\text{Gd} > \text{Tb} > \text{Dy} > \text{Y} > \text{Ho} > \text{Er} > \text{Tm}$).²¹ Therefore, $\text{Cr}:\text{GdAlO}_3$ is expected to delay thermal quenching of the spin-allowed broadband emission to higher temperatures than the other perovskite candidates. It should be noted that while the spin-forbidden luminescence from the perovskite $\text{Cr}:\text{YAlO}_3$ for temperature sensing has been previously reported,²² measurements were only made up to 75°C and no attempt was made to utilize its spin-allowed broadband emission at shorter wavelengths.

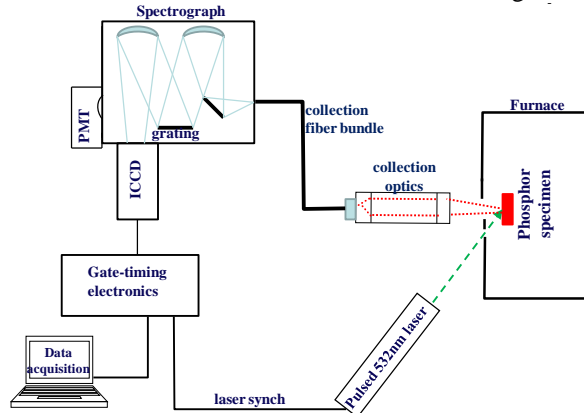


Figure 2. Time-resolved luminescence emission setup.

EXPERIMENT

Specimens were 25.4-mm diameter disks produced by sintering $\text{Cr}:\text{GdAlO}_3$ powder with a formula of $\text{GdAl}_{0.998}\text{Cr}_{0.002}\text{O}_3$, for a 0.2% Cr^{3+} cation doping level. Time-averaged and time-resolved luminescence emission spectra were collected using the experimental arrangement shown in Fig. 2. The specimen was placed inside a box furnace with two access holes in the back. Excitation by a pulsed 20 Hz, 532 nm (frequency double YAG:Nd) laser was transmitted through one of the access holes while luminescence emission was collected by a collection optics assembly with a 125 mm working distance through the other access hole. Fig. 3 shows an excitation spectrum obtained from a $\text{Cr}:\text{GdAlO}_3$ specimen, showing the choice of the 532 nm excitation was from a very wide range of excitation wavelengths that could be selected. The collected luminescence emission was transmitted via a fiber optic cable to a spectrograph, where time-resolved spectra were acquired by an intensified CCD (ICCD) camera or time-averaged spectra were acquired by a photomultiplier tube (PMT) through a slit. After an optimum wavelength range was selected, luminescence decay measurements were obtained by replacing the spectrograph with the appropriately selected bandpass filter in front of a PMT.

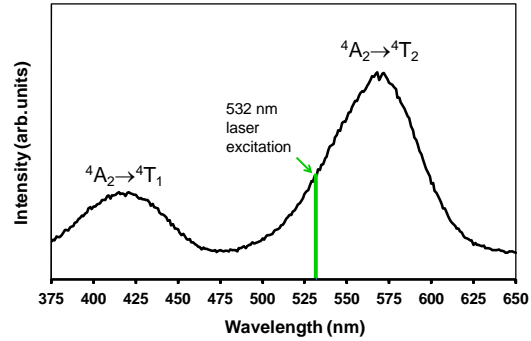


Figure 3. Room temperature excitation spectrum for $\text{Cr}:\text{GdAlO}_3$. Emission at 728 nm.

RESULTS

Fig. 4 shows the time-averaged luminescence emission spectra of a $\text{Cr}:\text{GdAlO}_3$ specimen as a function of temperature. It is evident from these spectra that the broadband emission centered at 640 nm becomes more prominent while the spin-forbidden R-line emission at 728 nm and the Stokes phonon-loss peak at 700 nm become less prominent with increasing temperature. It is also apparent that at the highest temperatures ($>700^\circ\text{C}$), the shorter-wavelength broadband emission dominates the emission spectra and therefore is the only component of luminescence emission remaining that can be used for temperature measurements.

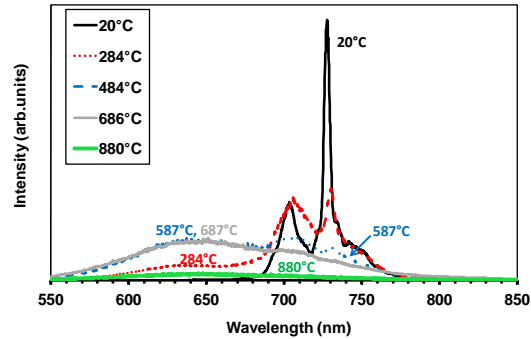


Figure 4. Temperature dependence of luminescence emission spectra for $\text{Cr}:\text{GdAlO}_3$. Excitation at 532 nm.

Time-resolved luminescence emission spectra at increments of delay after the laser excitation pulse were collected over a temperature range from room temperature to 1072°C . Examples of series of time-resolved spectra are shown for 378°C and 1072°C in Figs. 5-6. Fig. 5a shows the decay of the mixture of sharp R-line emission and broadband emission at 378°C . The same data is re-presented as a series of decay measurements at different wavelengths with a logarithmic intensity scale in Fig. 5b. The uniform downward slope across the full wavelength range (570-850 nm) in Fig. 5b suggests the same exponential

decay for all wavelengths within this range, i.e., $\tau_{2E} = \tau_{4T_2}$, as expected for thermal equilibrium between the 2E and 4T_2 populations. To provide a more quantitative indication of the decay rate uniformity across the full emission spectra, exponential decay constants were determined by nonlinear regression for six wavelength intervals starting with 570-600 nm and followed by 50-nm-span intervals up to 850 nm. At 378°C, averaging the determined decay constants from these wavelength intervals gave a mean of 3.85 msec with a standard deviation of ± 0.05 msec (corresponds to about $\pm 2^\circ\text{C}$). At 1072°C, the mean of the decay rate was 1.45 μsec with a standard deviation of ± 0.11 μsec (corresponds to about $\pm 5^\circ\text{C}$). The significance of this uniform decay behavior is that the decay-time/temperature calibration is insensitive to the choice of emission wavelength. This allows considerable flexibility in emission wavelength range selection, which can therefore be determined purely by consideration of signal intensity and avoidance of competing thermal radiation background. Fig. 6a displays the time-resolved spectra acquired at 1072°C, with only broadband emission remaining at this temperature. Fig. 6b, replotted as a series of decay curves at different wavelengths on a logarithmic intensity scale, shows a uniform luminescence decay rate for the broadband luminescence emission at 1072°C.

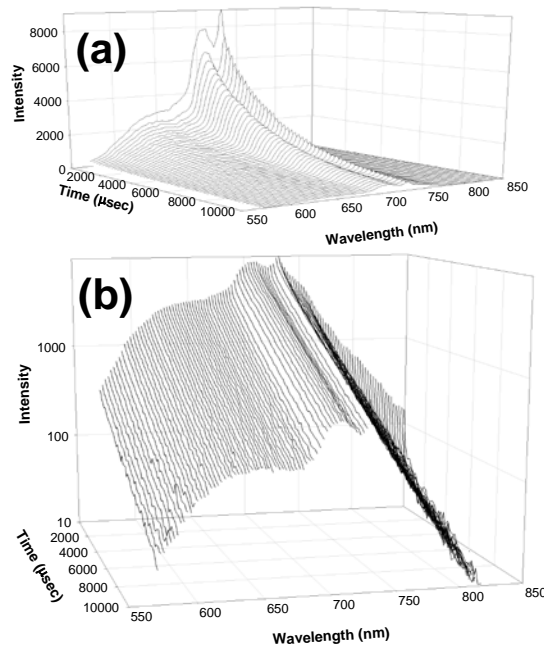


Figure 5. 3D plots showing time-resolved decay of luminescence emission spectra from Cr:GdAlO₃ at 378°C. (a) Linear intensity scale. (b) Logarithmic intensity scale shows uniform slope over full wavelength range, indicating wavelength-independent decay time.

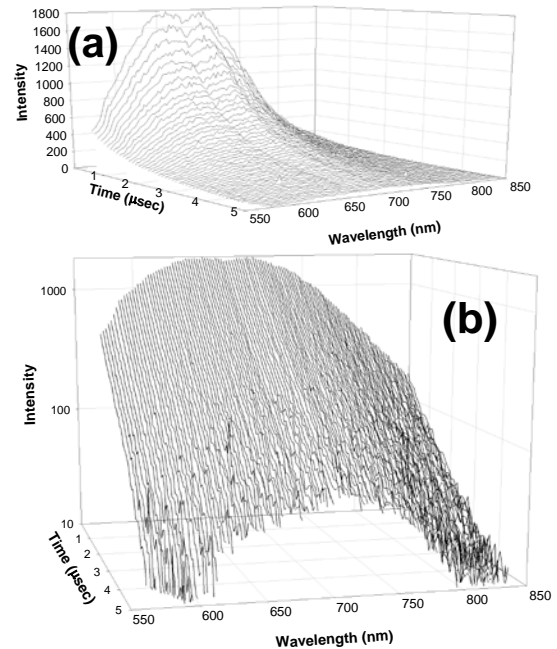


Figure 6. 3D plots showing time-resolved decay of luminescence emission spectra from Cr:GdAlO₃ at 1072°C. (a) Linear intensity scale. Only broadband emission remains. (b) Logarithmic intensity scale shows uniform slope over full wavelength range, indicating wavelength-independent decay time.

Fig. 6b shows that while the signal intensity at the short wavelength end of the range (570 nm) is substantially lower than at the peak intensity at 640 nm, there is still more than adequate signal intensity at 570 nm (where interference by background thermal radiation is much lower) to accurately determine the luminescence decay constant. Because of the wavelength-independent decay behavior, spectral information is unnecessary for obtaining reliable decay constants. Therefore, luminescence decay calibration data were obtained using a PMT with a bandpass filter to take advantage of the much greater light throughput compared to spectrograph acquisition. A bandpass filter centered at 590 nm with a full-width half-max of 40 nm was selected as a good compromise between collecting a wide wavelength range for greater signal while avoiding thermal radiation background at longer wavelengths. Luminescence decay curves acquired at various temperatures up to 1076°C using this bandpass filter are shown in Fig. 7. Although these decay curves are nearly single exponential, they were fitted by a double exponential equation due to a short, fast initial decay: $I = I_1 e^{-t/\tau_1} + I_2 e^{-t/\tau_2}$, where I is the intensity, t is time, τ_1 is the time constant associated with the short initial decay, and τ_2 is the time constant associated with the dominant long-term decay. The values of τ_2 were used for temperature calibration.

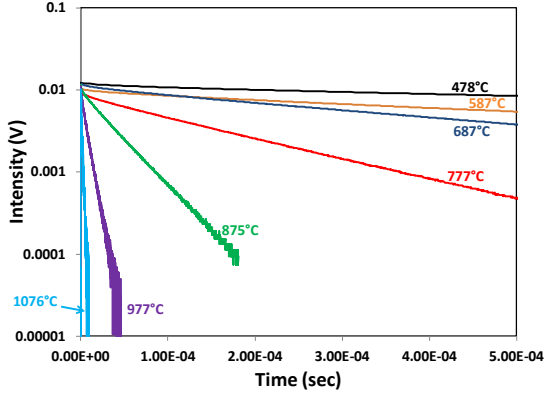


Figure 7. Luminescence decay at various temperatures from Cr:GdAlO₃. Using bandpass filter centered at 590 nm with a full-width half-max of 40 nm.

Based on the determined decay constants, a calibration between decay time and temperature up to 1075°C (the furnace limit) is shown in Fig. 8. These decay time vs. temperature data were in turn fitted by Equation 1, with fitting parameters τ_{2E}^R , ΔE , ΔE_q , $\ln(\alpha)$, and $\ln(\beta)$. The solid line in Fig. 8 is the fit of Equation 1 to the data using the Levenberg-Marquardt nonlinear least squares regression method, where to adequately weight the agreement between the data and the fit for the small decay values (decay values spanned four decades), the residuals were taken as the differences between the natural logarithms of the data and fit values.² The parameter values produced by this fit are listed in Table 1. Fig. 8 shows that a short extrapolation of the fit predicts decay times of 1.1 μ sec at 1100°C and 310 nsec at 1200°C.

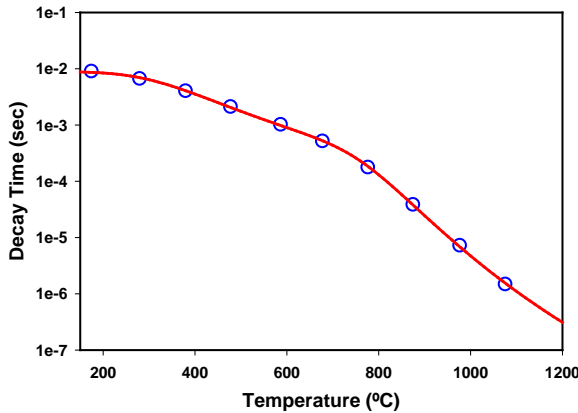


Figure 8. Temperature dependence of Cr:GdAlO₃ luminescence decay time for wavelengths selected by bandpass filter centered at 590 nm with a full-width half-max of 40 nm. Circles are values determined from measurements. Solid line is obtained by fitting Equation 1 to the data.

Table 1. Parameters determined by fitting Equation 1 to data in Fig. 8.

τ_{2E}^R (msec)	τ_{4T2}^R (μ sec)	τ_q (sec)	ΔE (cm ⁻¹)	ΔE_q (cm ⁻¹)
8.90	2.67	5.9×10^{-15}	3600	14525

DISCUSSION

The exceptional persistence of the spin-allowed broadband luminescence from Cr:GdAlO₃ to surprisingly high temperatures can be attributed to the strong crystal field the Cr³⁺ dopant ion experiences where it substitutes for the Al³⁺ ions inside the AlO₆ octahedra within the orthorhombic perovskite structure. In particular, the strong crystal field results in both a large ΔE between the ⁴T₂ and underlying ²E levels and also a large activation barrier, ΔE_q , against non-radiative crossover to the ⁴A₂ ground state (Fig. 1). The effects of the large ΔE and ΔE_q values are observed in the temperature dependence of the decay behavior shown in Fig. 8, and are effectively modeled by Equation 1. There appear to be two distinct regimes of luminescence decay, as previously reported for Cr:Al₂O₃ and other high crystal field hosts.^{23,24} The first, more slowly decreasing regime observed in Fig. 8 is from about 200 to 750°C, and can be attributed to the effect of the thermal population of the ⁴T₂ level at the expense of the ²E reservoir population. This population shift to the higher ⁴T₂ level occurs with no decrease in radiative efficiency, and the observed decay time decreases because a greater fraction of the radiative decay occurs from the much shorter-lived ⁴T₂ level. One of the beneficial consequences of this shift is that more of the luminescence is produced at the shorter wavelengths associated with the broadband emission where there is less interference from thermal background radiation than for the R-line emission at 728 nm. The second, more steeply decreasing decay regime starts at about 750°C where the effects of non-radiative crossover from the ⁴T₂ to ⁴A₂ levels become a significant alternate relaxation pathway, reducing both radiative efficiency and decay time. While both these regimes and underlying mechanisms have been described for other Cr-doped phosphors, the higher values of ΔE and ΔE_q for Cr:GdAlO₃ extend these regimes to much higher temperatures. For example, the estimated value of ΔE for Cr:GdAlO₃ is 3600 cm⁻¹, considerably higher than the 2350 cm⁻¹ value for Cr:Al₂O₃.⁷ The higher ΔE delays the thermal depopulation from the ²E reservoir to higher temperatures. Based on the much higher ΔE value for Cr:GdAlO₃, the fraction of excited Cr³⁺ ions that

populate the 4T_2 level of Cr:GdAlO₃ will be much lower than for Cr:Al₂O₃ at the same temperature. Therefore, the equivalent thermal promotion of Cr³⁺ ions to the 4T_2 level will be delayed to substantially higher temperatures for Cr:GdAlO₃; for example, the fraction of excited Cr³⁺ ions that populate the 4T_2 level of Cr:GdAlO₃ will not reach the fraction obtained for Cr:Al₂O₃ at 600°C until Cr:GdAlO₃ reaches 1060°C. Similarly, a higher ΔE_q delays the thermal quenching by non-radiative crossover to higher temperatures.

In summary, the spin-allowed broad luminescence emission from the Cr:GdAlO₃ exhibits considerable advantages for performing luminescence-decay-based temperature measurements up to 1200°C. Typical of transition metal dopant phosphors, this phosphor offers intense luminescence and a flexible selection of excitation wavelengths, and the utilization of the spin-allowed broadband emission allows for a flexible selection of emission wavelengths. The most novel attribute of this phosphor is the unusual persistence of sufficiently long-lived spin-allowed broadband emission to higher temperatures. Selection of the shorter emission wavelengths associated with the broadband emission provides the additional benefit of reduced interference from interfering thermal radiation background. In particular, Cr:GdAlO₃ will be preferred over weaker-intensity rare-earth-doped phosphors, such as Dy:YAG, at temperatures up to 1200°C for intensity-starved situations when the much lower emission intensity from rare-earth-doped phosphors is insufficient for accurate temperature measurements in the presence of significant radiation background.

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