

RARE EARTH GARNET SELECTIVE EMITTER

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ABSTRACT

Thin film Ho-YAG and Er-YAG emitters with a platinum substrate exhibit high spectral emittance in the emission band ($\epsilon_\lambda \approx 0.75$, $^4I_{15/2} - ^4I_{13/2}$, for Er-YAG and $\epsilon_\lambda \approx 0.65$, $^5I_7 - ^5I_8$ for Ho-YAG) at 1500K. In addition, low out-of-band spectral emittance, $\epsilon_\lambda < 0.2$, suggest these materials would be excellent candidates for high efficiency selective emitters in thermophotovoltaic (TPV) systems operating at moderate temperatures (1200-1500K). Spectral emittance measurements of the thin films were made ($1.2 < \lambda < 3.0 \mu\text{m}$) and compared to the theoretical emittances calculated using measured values of the spectral extinction coefficient.

In this paper we present the results for a new class of rare earth ion selective emitters. These emitters are thin sections ($< 1\text{mm}$) of yttrium aluminum garnet (YAG) single crystal with a rare earth substitutional impurity. Selective emitters in the near IR are of special interest for thermophotovoltaic (TPV) energy conversion^{1,2}. The most promising solid selective emitters for use in a TPV system are rare earth oxides. Early spectral emittance work³ on rare earth oxides showed strong emission bands in the infrared (.9 - 3 microns). However, the emittance outside the emission band was also significant and the efficiency of these emitters was low. Recent improvements in efficiency^{4,5} have been made with emitters fabricated from fine (5-10 μm) rare earth oxide fibers similar to the Welsbach mantle used in gas lanterns. However, the rare earth garnet emitters are more rugged than the mantle type emitters.

A thin film selective emitter⁶ on a low emissivity substrate such as gold, platinum etc., is rugged and easily adapted to a wide variety of thermal sources. The garnet structure and its many subgroups have been successfully used as hosts for rare earth ions, introduced as substitutional impurities, in the development of solid state laser crystals⁷. Doping, dependent on the particular ion and crystal structure, may be as high as 100 at. % (complete substitution of yttrium ion with the rare earth ion). These materials have high melting points, 1940 C for YAG (Yttrium Aluminum Garnet), and low emissivity in the near infrared making them excellent candidates for a thin film selective emitter.

As previously stated, the spectral emittance of a rare earth emitter is characterized by one or more well defined emission bands. Outside the emission band the emittance(absorptance) is much lower. Therefore, it is expected that emission outside the band for a thin film selective emitter will be dominated by the emitter substrate. For an efficient emitter (power in the emission band/total emitted power) the substrate must have low emittance, ϵ_s . Within the emission band the spectral emittance is governed by the index of refraction, n_f , and the spectral extinction coefficient, α_λ (sum of the absorption coefficient, a_λ , and scattering coefficient, σ_λ), the emitter temperature, T_E , and thickness, d . In reference 6 the emitter emittance and efficiency are derived as a function of the optical depth, $K_\lambda = \alpha_\lambda d$, and the dimensionless emission-band energy, E_g/kT_E , where E_g is the photon energy at the center of the emission band. This analysis shows that maximum efficiency occurs for an optimum K_λ and $E_g/kT_E \sim 4$.

This paper presents normal spectral emittance, ϵ_λ , measurements of holmium, (Ho) and erbium (Er) doped YAG thin film selective emitters at (1500 K), and compares those results with the theoretical spectral emittance. The spectral extinction coefficient, which is required to calculate ϵ_λ , was also

calculated from transmission and reflectance measurements performed at room temperature.

Specimens were cut from Czochralski grown crystals and polished on both sides with 1 μ diamond abrasive. Spectral transmission, T_λ , and reflectance, R_λ , measurements were made at room temperature with a Perkin Elmer Lambda 19 UV/VIS/NIR spectrophotometer and a Nicolet Model 750 Magna-IR spectrometer. The spectral extinction coefficient, α_λ , was calculated⁸ using:

$$e^{-\alpha_\lambda d} = \frac{1}{2} \left\{ \sqrt{\left[\frac{(1-R_\lambda)^2 - T_\lambda^2}{T_\lambda^2} \right]^2 + 4} - \frac{1}{T_\lambda} [(1-R_\lambda)^2 - T_\lambda^2] \right\} \quad (1)$$

Fig. 1 shows the spectral extinction coefficient for 25 at. % Ho-YAG (.32 mm thickness) and 40 at. % Er-YAG (.65 mm thickness) specimens within the emission band. Relatively strong absorption is evident at the characteristic laser transitions in Er-YAG ($^4I_{15/2} - ^4I_{13/2}$) and Ho-YAG ($^5I_7 - ^5I_8$). Measurements with the Nicolet Model 750 Magna-IR spectrometer indicate the absorption is low compared to the emission band in the near infrared until approximately $\lambda = 6\mu$ where absorption increases greatly and continues through the far infrared.

Quantities such as emissivity and absorptivity are usually thought of as properties of an isothermal surface. However, for the thin film rare-earth YAG emitter emission from throughout the film contributes to the spectral emittance. Since significant temperature gradients (200 K) exist across the specimens the "emitter temperature", used to calculate emittance from the intensity measurements, is not the surface temperature but rather the average of the front and back surface temperatures in the center of the sample. Temperature measurements, made with type R thermocouples, had an accuracy of +/- 6K. Spectral intensity measurements were made with a monochromator and a temperature controlled PbS detector calibrated with a 1270 K blackbody reference. Measurement accuracy and repeatability with the blackbody standard at 1270 K were typically within 2%. Platinum foil was placed behind the samples as a low emittance substrate. The configuration shown in fig. 2 was used to eliminate reflected radiation from the furnace interior, a near blackbody radiator, from reaching the detector. Two sources of measurement error were identified. Alumina insulation, a nearly perfect diffuse reflector, reflects radiation originating from the perimeter of the sample (a), which is at a higher temperature than the viewed area, to the surface of the sample in the field of view of the detector. Also, emission from the hot alumina (b) is reflected directly from the viewed area to the detector. Comparison of ϵ_λ measurements of platinum foil under conditions identical to those required to produce an average emitter temperature of 1500 K (furnace @ 1664 K) and data from ref. 9 show the increase in ϵ_λ due to reflected radiation is +0.09 @ 2.0 μ m and +0.125 @ 1.5 μ m. This will be the maximum measurement error for materials with high spectral reflectance (~80 %) and low emittance such as platinum. However, in the Ho and Er-YAG specimens, reflectance in the emission band is less (20-70% for Ho-YAG). Therefore, an estimate for the maximum experimental error in measured values of ϵ_λ in the emission band is +/- 0.1.

Fig. 3 shows the measured and theoretical⁶ spectral emittance for different values of the scattering albedo, $\Omega_\lambda = \sigma_\lambda / (a_\lambda + \sigma_\lambda)$, of 25% Ho-YAG (.65 mm thickness) and 40% Er-YAG (1.04 mm thickness) at 1500 K. The theory assumes a uniform temperature for the film and the theoretical spectral emittance is independent of temperature. For theoretical calculations the extinction coefficients shown in fig.1 were used. An index of refraction of $n_f = 1.9$ was used for the rare-earth YAG and the platinum substrate was assumed to have a constant spectral emittance⁹ of $\epsilon_s = 0.2$. Small changes in n_f (<0.1) had a negligible effect on the theoretical results. In comparing the theoretical and experimental ϵ_λ results, several features should be noted. First, results with small scattering ($\Omega_\lambda < 0.5$) agree more closely with the measurements. Second, the measured emittance outside the emission band is considerably higher than the theoretical values. As stated earlier, emission outside of the band is primarily from the platinum substrate. Measurements of ϵ_λ of pure platinum foil under identical conditions required to produce an average emitter temperature of 1500 K provided a value of 0.28 @ 2.4 μ m. This value corresponds well

with the out of band emission observed in fig. 3a,b. Values of experimental ϵ_λ for the platinum substrate are greater than ref. 9 due to reflected radiation seen by the detector. Finally, due to absorption in the rare-earth YAG, theoretical values for ϵ_λ outside the emission band are less than the substrate emittance, $\epsilon_s = 0.2$.

In conclusion, we have measured large emittance in the emission band of Ho-YAG, $\epsilon_\lambda \approx .65$, and Er-YAG, $\epsilon_\lambda \approx .75$, thin film selective emitters. Calculated spectral emittances for small scattering ($\Omega_\lambda < .5$) are in fairly good agreement with the measured emittances. However, accurate emittance calculations are possible only if the temperature gradient across the thin emitter is included. Finally, the large emittance in the emission band and low out-of-band emittance suggest that Ho-YAG and Er-YAG thin film selective emitters may make it possible to develop an efficient TPV energy conversion system at moderate temperatures (1500K).

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REFERENCES

1. R. E. Nelson and P. A. Iles, ASME/ASES/SOLTECH Joint Solar Energy Conference, (1993)
2. P. A. Iles, Conference Record of 21st IEEE Photovoltaic Specialists Conference, 420 (1990)
3. G.E. Guazzoni, Appl. Spectra **2** 6, 60 (1972)
4. R.E. Nelson, Proceedings of the 32nd International Power Sources Symposium, 95 (1986)
5. C.R. Parent and R.E. Nelson, Proceedings of the Twenty-First Intersociety Energy Conversion Engineering Conference, 1314 (1986)
6. D. L. Chubb and R. A. Lowe, J. Appl Phys. **7** 4 (9), 5687 (1993)
7. L.G. DeShazer, S.C. Rand, and B.A. Wechsler, *CRC Handbook of Laser Science and Technology, Vol. 5, Part 3, "Laser Crystals"*, (CRC Press) 1987
8. R. Siegal and J. R. Howell, *Thermal Radiation and Heat Transfer*, (Hemisphere, Washington, DC) 2nd ed. 1981, p. 722
9. Y.S. Touloukian and C.Y. Ho, *Thermophysical Properties of Matter vol. 7 "Thermal Radiative Properties Metallic Elements & Alloys"*, (IFI/Plenum, New York-Washington) 1970, p. 542 (curve 39)

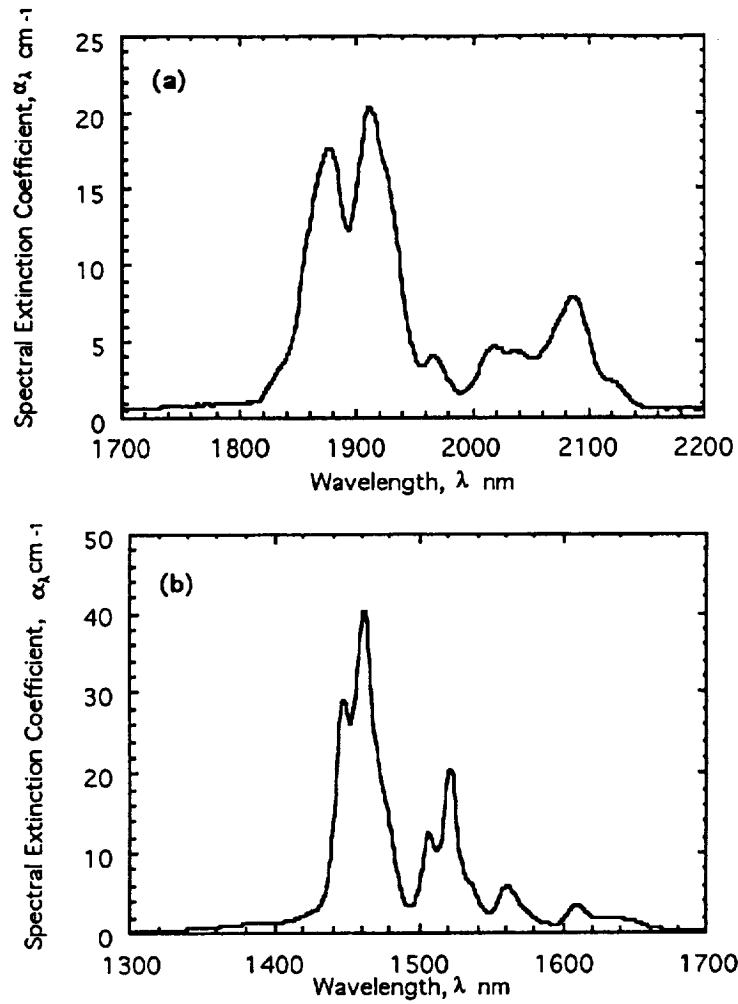


FIG. 1 Spectral extinction coefficient calculated from measured transmission and reflectance (a) 25% Ho-YAG (b) 40% Er-YAG

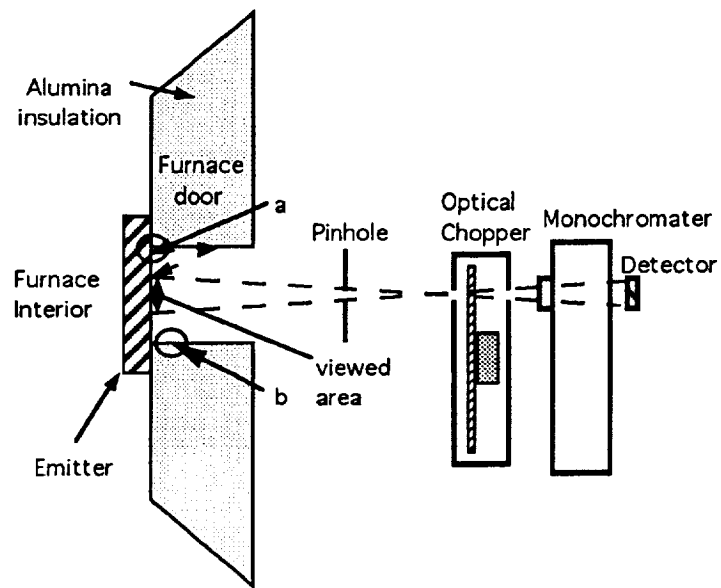
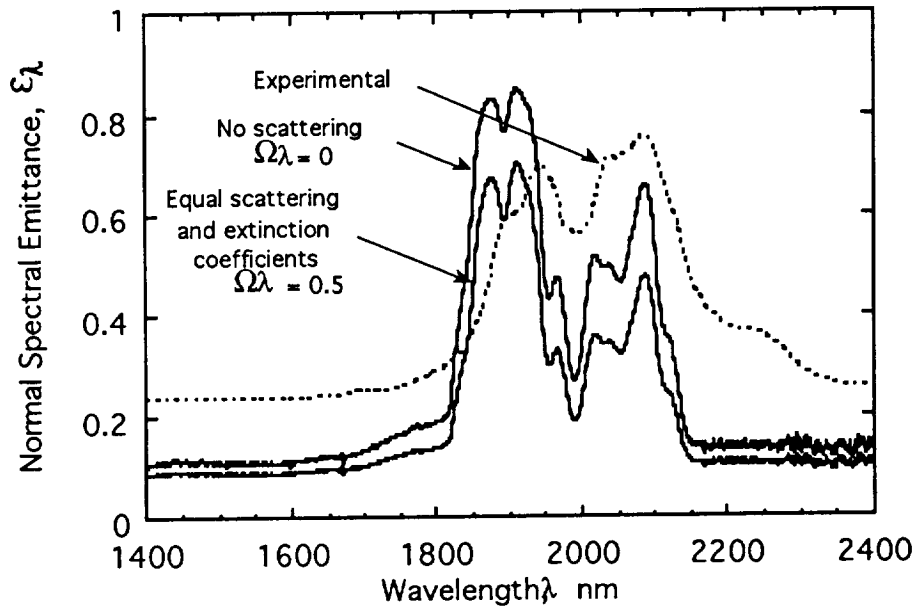
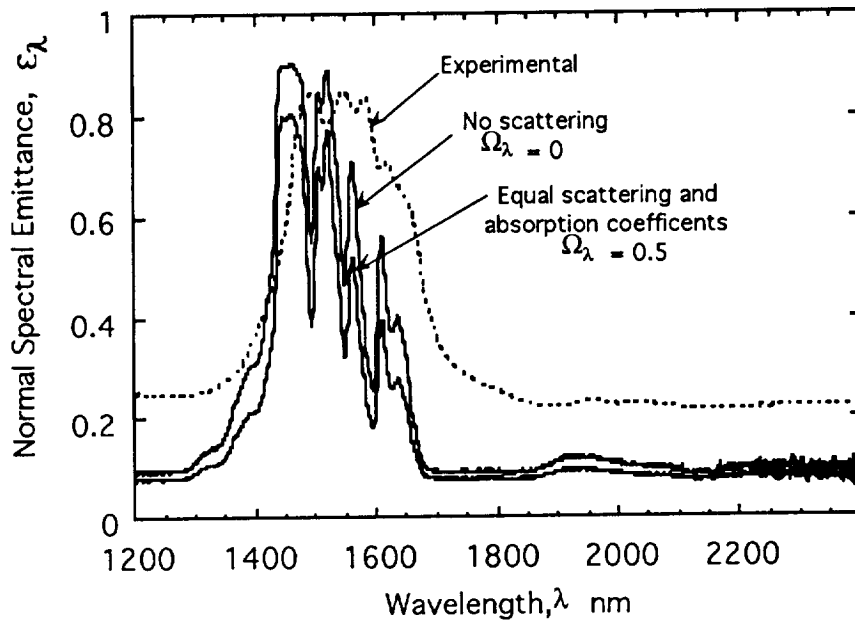


FIG. 2 Schematic representation of the experimental setup



(a)



(b)

FIG. 3 Theoretical and measured spectral emittance ϵ_λ with a platinum foil substrate (constant $\epsilon_\lambda = .2$) and index of refraction for YAG ($n_f = 1.9$) used for theoretical calculations (a) 25% Ho-YAG .65 mm thick; front surface temp. = 1389 K, back surface temp. = 1616K, average emitter temp. = 1500K (b) 40% Er-YAG 1.04 mm thick; front surface temp. = 1398K, back surface temp. = 1606K, average emitter temp. = 1500K

