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mately 2. Experimentally we have found that  $R$  has the value of unity or slightly greater, within a maximum experimental error of  $\pm 0.2$ . There is no significant variation in this value between focused and unfocused input beams, so spatial non-overlap cannot be a factor. Pulse envelope traces (Tektronix 519 oscilloscope) of the laser output show regular modulation indicating some locking of the multimodes. While this would increase the efficiency of S.H.G.,<sup>12</sup> it would require for the mixing process a more critical synchronization of the resulting modulation of the two fundamental frequencies. Streak interferograms (2 nsec resolution) show that such complete synchronization does not exist.

After this work had been completed, the mixing of ruby and neodymium  $Q$ -switched lasers operating in a common resonator to produce a summed output at 4192 Å was reported<sup>13</sup> but the relative efficiencies of S.H.G. and sum generation were not compared.

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## A NEW PHOSPHOR FOR FLYING-SPOT CATHODE-RAY TUBES FOR COLOR TELEVISION: YELLOW-EMITTING $Y_3Al_5O_{12}-Ce^{3+}$

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(Received 29 May 1967)

The fluorescence of  $Y_3Al_5O_{12}-Ce^{3+}$  under cathode-ray excitation consists of an emission band peaking at 550 nm. The decay time is 0.07–0.08  $\mu$ sec. In view of these properties this phosphor is very suitable for flying-spot cathode-ray tubes for color television.

$Ce^{3+}$ -activated phosphors are usually characterized by an emission band with a maximum in or near the uv region and a very short decay time.<sup>1</sup> In this Letter we report on a  $Ce^{3+}$ -activated phosphor with an emission at considerably longer wavelengths, viz.  $Y_3Al_5O_{12}-Ce$ .

Samples with the general formula  $Y_{3-x}Ce_xAl_5O_{12}$  ( $x < 0.3$ ) were prepared by firing intimate mixtures of high-purity  $Y_2O_3$ , hydrated alumina and  $Ce_2O_3$  at 1500° in nitrogen. X-ray analysis showed them to be pure garnets. According to chemical analysis the  $Ce^{4+}$  content of the samples is negligible. This was also the case if the samples were fired in oxygen, air, or nitrogen containing 5% of hydrogen. Optical measurements were performed as described previously.<sup>2</sup>

$Y_3Al_5O_{12}-Ce$  shows a bright yellow emission

under excitation with cathode rays as well as with blue radiation. Figure 1 shows the spectral energy

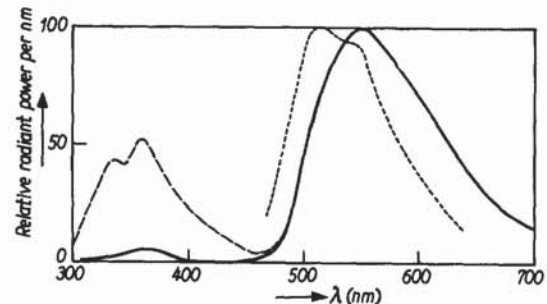


Fig. 1. Spectral energy distribution of  $Y_{2.94}Ce_{0.06}Al_5O_{12}$  under cathode ray excitation (full line), uv excitation (broken line) and of  $Y_{2.94}Ce_{0.06}Al_2Ga_3O_{12}$  under uv excitation (dotted line). The solid and broken lines coincide in the visible region.

distribution of the emission of  $Y_3Al_5O_{12}-Ce$  under cathode-ray (cr) as well as under ultraviolet (uv) excitation. Figure 2 shows the excitation spectrum of the visible fluorescence of  $Y_3Al_5O_{12}-Ce$  and the diffuse reflection spectra of  $Y_3Al_5O_{12}-Ce$  and unactivated  $Y_3Al_5O_{12}$ . The radiant efficiency for cr excitation (20 keV) is 3.5% for the emission in the visible region and 0.1% for the emission in the uv region.<sup>3</sup> These figures were found for a sample with composition  $Y_{2.94}Ce_{0.06}Al_5O_{12}$  and vary only slightly with the Ce concentration. At very low Ce concentration the ratio of the intensities of uv to visible emission increases.

Decay times were measured with cr and uv excitation. With cr excitation the phosphor was irradiated with short electron beam pulses (duration 0.1  $\mu$ sec, repetition rate  $10^4$  cps) in a demountable tube. The fluorescence was collected on a photomultiplier and displayed on an oscilloscope. The decay time was found to be shorter than 0.1  $\mu$ sec. The phosphor was also excited by a short pulse of uv radiation with the aid of a TRW nanosecond spectral source system (duration 0.004  $\mu$ sec, repetition rate  $5 \times 10^3$  cps). The output was again displayed on an oscilloscope. The decay time proved to be 0.07–0.08  $\mu$ sec.

All  $Ce^{3+}$ -activated phosphors described in the literature show the maximum of their emission in the uv or blue (up to  $\approx 410$  nm). The emission from  $Y_3Al_5O_{12}-Ce$  under cr excitation, however, lies almost entirely in the visible with a broad band peaking at 550 nm. There is also a uv emission band under short-wave uv excitation. In view of this peculiar behavior it may be wondered whether this emission is really due to the  $Ce^{3+}$  center. There are several reasons for believing that this is the case:

(a) Chemical analysis excludes other oxidation states of cerium; (b) unactivated  $Y_3Al_5O_{12}$  does not

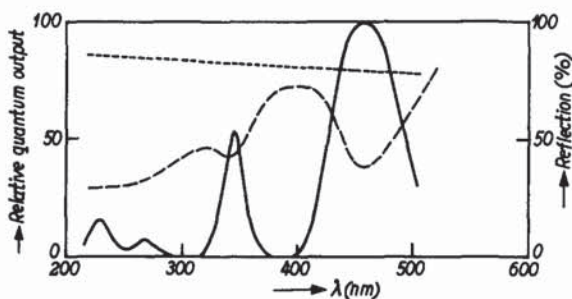


Fig. 2. Relative excitation spectrum of the visible fluorescence of  $Y_{2.94}Ce_{0.06}Al_5O_{12}$  (solid line) and diffuse reflection spectra of  $Y_{2.94}Ce_{0.06}Al_5O_{12}$  (broken line) and  $Y_3Al_5O_{12}$  (dotted line).

emit in this region; (c) the decay time of  $Ce^{3+}$  phosphors is always very short, viz. shorter than 0.1  $\mu$ sec, since an allowed transition is involved ( $^2D \rightarrow ^2F$ ).  $Y_3Al_5O_{12}-Ce$  has such a short decay time; (d) the emission band of  $Ce^{3+}$  phosphors should consist of two bands, the ground state being split ( $^2F_{7/2}, ^2F_{5/2}$ ). The energy difference between these two bands is some  $2000\text{ cm}^{-1}$ . Particularly at higher Ce concentrations this splitting is not always observed. The uv emission band of  $Y_3Al_5O_{12}-Ce$  does indeed exhibit two peaks (29,800 and 27,800  $\text{cm}^{-1}$ ) but the visible band does not.  $Y_3Al_2Ga_3O_{12}-Ce$  with similar but less efficient fluorescence, however, shows an indication of the splitting of this emission band in the visible.

Figure 2 shows that  $Y_3Al_5O_{12}-Ce$  is most efficiently excited by 460 nm radiation. The efficiency for long-wave uv excitation is less, and that for short-wave uv excitation may even be termed low. The excitation bands correspond to absorption in the  $Ce^{3+}$  center. This follows from a comparison between the diffuse reflection spectra of  $Y_3Al_5O_{12}$  and  $Y_3Al_5O_{12}-Ce$ . These bands show the complete crystal field splitting of the  $^2D$  level of  $Ce^{3+}$ .

Elsewhere we will discuss this and other  $Ce^{3+}$  phosphors more extensively. For the moment we conclude that  $Y_3Al_5O_{12}-Ce^{3+}$  is an exceptional  $Ce^{3+}$  phosphor with an emission at relatively long wavelengths and a high efficiency under cr excitation.

Therefore this phosphor can be of use for flying-spot cathode-ray tubes, especially for color television. When the screen of such a tube is scanned with a normal television raster, a decay time of the phosphor shorter than  $\approx 0.1\ \mu$ sec is required. Usually ZnO-Zn is used with an emission band at 500 nm containing only a small amount of red and with an efficiency which is about the same as that of  $Ce^{3+}$ -activated phosphors. Its decay time, however, is too long, viz.  $\approx 1\ \mu$ sec. Therefore a large correction is applied to the output signal by electrical compensation with unavoidably a great reduction in this signal.  $Y_3Al_5O_{12}-Ce$  has a much higher output in the red region and, moreover, a much shorter decay time. Therefore the output signal of this tube is expected to be an order of magnitude higher than for ZnO-Zn. The emission of  $Y_3Al_5O_{12}-Ce$  does not contain blue. However, efficient blue phosphors with short decay time are available (for example,  $Ca_2Al_2SiO_7-Ce$  (ref. 1)), so that a mixture of these two phosphors will suffice.

<sup>1</sup>See, e.g., A. Brill and H. A. Klasens, *Philips Res. Repts.* 7, 421 (1952).

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<sup>3</sup>For comparison: the most efficient  $Ce^{3+}$ -activated phosphor  $Ca_2Al_2SiO_7$  has an efficiency of 4% (ref. 1).

## HIGH TEMPERATURE RESONANCE LOSSES IN SILICON-DOPED YTTTRIUM-IRON GARNET (YIG)\*

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The ferrimagnetic resonance linewidth of silicon-doped YIG, measured as a function of temperature at 13.4 kHz, is found to show a pronounced peak at 105°C. The anisotropic behavior of this peak is in good agreement with the four-level valence-exchange model proposed by Clogston. The model yields for the electron ordering energy a value  $5 \times 10^{-4}$  eV which agrees closely with the energy deduced from magnetic anneal studies. The activation energy for electron transfer (0.25 eV) is virtually identical with values reported in investigations of electrical conductivity and acoustic loss.

It is known that the introduction of small concentrations of silicon into the YIG lattice leads to a significant increase in magnetic loss. There is general agreement, however, that silicon itself plays only an incidental role and that the losses are actually due to the presence of divalent iron created in response to the addition of quadrivalent silicon.

In YIG samples containing  $Fe^{2+}$  two peaks have been reported in the plot of microwave resonance linewidth vs temperature. Typically, one peak occurs at low temperature below ca. 100°K, and the other above ca. 300°K. It was suggested, at the time of its discovery, that the low temperature peak was due to valence exchange,<sup>1,2</sup> i.e., electron transfer between  $Fe^{2+}$  and  $Fe^{3+}$  cations. More recently, Tchernev<sup>3</sup> has argued that the electron-hopping mechanism is, in all likelihood, "frozen out" at temperatures below 100°K, and therefore, it is more reasonable to ascribe the peak to the localized  $Fe^{2+}$  ion acting, more or less,<sup>4</sup> as a slow relaxer. The high temperature peak has been looked at to a

lesser extent<sup>5,7</sup> and the suggestion has been made that it is due to valence exchange.<sup>7</sup>

In our work the temperature dependence and anisotropy of the upper peak have been examined in some detail. Our results provide strong evidence that the high temperature resonance losses are, indeed, due to valence exchange, a conclusion that would seem to exclude this mechanism as the one also responsible for the low temperature peak.

We have measured the linewidth of the uniform precession at 13.4 kHz for several single crystals of silicon-doped YIG ( $Y_3Fe_{5-\delta}Si_\delta O_{12}$ ) between room temperature and the Curie point. The crystals were grown from a PbO-PbF<sub>2</sub> flux using high purity starting materials to which controlled amounts of SiO<sub>2</sub> were added. Silicon concentration was determined from spectrographic analysis of several crystals (not the actual samples) selected from the growth run. Measurements were made on samples prepared as well polished spheres, 0.025" in diameter. These were mounted in a TE-108 transmission cavity and linewidth measurements were made using the half-power method.<sup>8</sup>

Our results for the composition  $\delta = 0.06$  are shown in Fig. 1. A sample containing a smaller silicon content ( $\delta = 0.04$ ) showed the same temperature dependence but with the magnitude of the losses reduced roughly in proportion to the doping,

\*The experimental work was performed under contract with the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

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