

Philips Journal of Research

Vol. 36 No. 1 1981



PHILIPS



**DOCKET
ALARM**

Find authenticated court documents without watermarks at docketalarm.com.

Philips Journal of Research

Philips Journal of Research, published by the Philips Research Laboratories, Eindhoven, The Netherlands, is a bimonthly publication containing papers on research carried out in the various Philips laboratories. Volumes 1 to 32 have appeared under the name of Philips Research Reports.

Annual subscription price for Volume 36 is Dfl. 70, payable in advance. Payments should be made only after receipt of an invoice. Correspondence should be addressed to: Philips Journal of Research, Philips Research Laboratories, Building WBp, Room No. 42, Eindhoven, The Netherlands.

Editor-in-chief: J. de Groot

Cover design based on a visual representation of the sound-wave associated with the spoken word "Philips".

COLOURSHIFT OF THE Ce^{3+} EMISSION IN MONOCRYSTALLINE EPITAXIALLY GROWN GARNET LAYERS

by J. M. ROBERTSON, M. W. VAN TOL, W. H. SMITS
and J. P. H. HEYNEN

Abstract

Starting with Ce-doped $Y_3Al_5O_{12}$ grown by liquid-phase epitaxy, the colour of the cerium emission was shifted by making various substitutions in the garnet lattice. The substitutions were made with the purpose of changing the crystal field acting on the Ce^{3+} ion in the garnet lattice. The light outputs and the colour points of the resulting phosphors have been measured and the influence of filtering away part of the emission has been calculated. It proves to be possible to obtain green and red phosphors with compatible light output and the right colour points for colour TV purposes.

1. Introduction

Recently it has been demonstrated that liquid-phase epitaxy (LPE) could be used to grow monocrystalline layers of garnets which could be used as screens in cathode ray tubes^{1,2,3}). In this manner it is possible to make miniature display tubes in which high excitation densities can be used (ca. 10 W/cm^2) without thermal quenching or "burning in" of the phosphor layer. The epitaxially grown $Ce^{3+}: Y_3Al_5O_{12}$ (YAG) gives a cathode ray efficiency of ca. 5%³) and has a high quenching temperature (310°C), however it has a broad band emission with maximum intensity at ca. 555 nm resulting in a colour which is too yellow to be used as a green component in a colour TV system. From the literature⁴) it is known that the emission band of the $Ce^{3+}: YAG$ can be shifted towards shorter wavelengths by substituting other ions into the garnet structure. In the present paper we shall show that it is possible to shift the Ce^{3+} emission in LPE grown YAG so that it has the desired colour coordinates for a green TV tube. We also investigated the possibility of making shifts in the emission so that blue and red tubes could be made by similar use of molecular engineering.

2. General method

The luminescent properties of Ce^{3+} doped phosphors have been studied in detail in ref. 5. In the ground state the Ce^{3+} ion has one electron in the 4f state.

The ground state is split up in a doublet ($^2F_{7/2}$ and $^2F_{5/2}$) with an energy difference of about 2200 cm^{-1} . At low temperatures this doublet results in two peaks in the emission band⁶); at room temperature it is one of the main causes of the width (at half maximum) of about 105 nm of the emission band. In the first excited state the electron occupies a 5d state. The interaction between the wave function of the electron in the 5d state and the crystal field results in a broadening of this state and in a splitting into five energy levels. The emission of the UV- or cathode ray excited Ce^{3+} ion is due to the transfer of an electron from the lowest 5d level to the 2F ground state; transitions from higher 5d states have a relatively low probability at room temperature owing to the strong interaction between the 5d states. A change in crystal field will give a larger or smaller splitting of the 5d state, which results in a shift of the emission spectrum to longer or shorter wavelengths. In most crystal structures the crystal field splitting is small and the Ce^{3+} ion shows an emission in the blue or UV, but as a consequence of the extraordinary large crystal field splitting in YAG, the Ce^{3+} ion emits in the green-yellow in this host lattice with a maximum intensity at 555 nm.

Holloway and Kestigian⁶) showed that if Lu^{3+} was substituted for Y^{3+} in YAG powders, the emission of the Ce^{3+} ion shifts to shorter wavelengths. Other workers^{7,8,9}) substituted Gd^{3+} or La^{3+} for Y^{3+} and shifted the emission to longer wavelengths, while the substitution of Ga^{3+} , In^{3+} or Sc^{3+} for Al^{3+} on an octahedral site shifted the Ce^{3+} emission to shorter wavelengths^{6,7,9}).

These results form the basis for the empirical rule, used in the present work: increasing the diameter of the ion on the dodecahedral (Y^{3+}) site increases the crystal field splitting, while an increasing diameter on the octahedral (Al^{3+}) site has the reverse effect. In this study double substitutions on both the dodecahedral and octahedral sites were investigated, as well as the substitution of a smaller ion on the tetrahedral (Al^{3+}) site.

3. Experimental techniques

The liquid-phase epitaxial growth technique, the cathodoluminescence efficiency measurement in a demountable cathode-ray system and the measurement of the spectra have been described in detail elsewhere³). The substrates on which the epitaxy was performed were $\text{Y}_3\text{Al}_5\text{O}_{12}$ (12.001 Å), $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (12.280 Å) and $\text{Y}_3\text{Al}_{3.5}\text{Ga}_{1.5}\text{O}_{12}$ (12.119 Å)¹⁰), usually 25 mm in diameter, 700 μm thick and cut and polished in [111] orientation.

The chemical analysis of the layers was performed with the help of an electron beam microprobe, calibrated against a set of carefully selected standards.

4. Results and discussion

4.a. Green shift

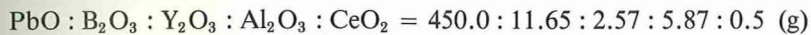
In order to have the right hue for the green component the emission must be shifted to the short wavelength side of the spectrum, which means that Lu and/or Ga must be substituted. If such a phosphor is to be grown epitaxially on a commercially available substrate (such as YAG), this substitution must result in a lattice parameter which differs less than 0.018 \AA from that of the substrate. This can be ensured by a simultaneous substitution of Lu^{3+} for Y^{3+} and Ga^{3+} for Al^{3+} in the correct ratio. Since the lattice parameters of YAG, LuAG and YGG are 12.001 , 11.908 and 12.280 \AA respectively, a simultaneous substitution of Lu and Ga gives

$$d(Y_{3-y}Lu_yAl_{5-x}Ga_xO_{12}) = 12.001 - 0.031y + 0.056x.$$

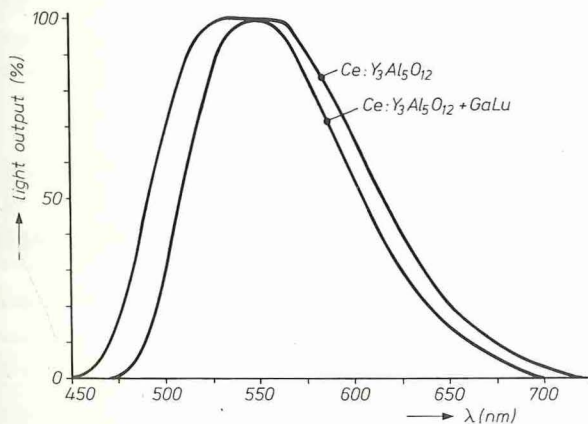
For no lattice mismatch between film and substrate (YAG), i.e. for good epitaxy, Lu^{3+} and Ga^{3+} must build in a ratio of 9:5.

The first experiment was set up to check this ratio and to establish whether the shift in the Ce emission is a linear function of the Lu and Ga substitutions and to investigate whether the effects of the substitutions are independent or not.

We started with a melt composition



and a growth temperature of ca. $1030 \text{ }^\circ\text{C}$. Lutetium oxide and Ga_2O_3 were added in consecutive steps so that the lattice parameter of the film was almost constant. Table I shows the results of light output (L), colour point and chemical analysis of the layers. The emission spectrum of sample 8 (doped with the



Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts



Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.