THE LUMINESCENCE EFFICIENCY OF YAG : Ce PHOSPHORS

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The luminescence intensity of Yttrium aluminium garnet activated by the Ce^{3+} (YAG : Ce^{3+}) under cathode-ray excitation depends on the preparation method and content of some dopants. Samples containing Fe, Pt, Ir or some colour centre, respectively, show relatively low luminescence. The maximum luminescence intensity was obtained with the Czochralski method grown single crystals in 98% Ar + 2% H_2 atmosphere which were sensitized by oxygen annealing followed by treatment at 1500 °C in molybdenum container using a wet hydrogen atmosphere.

1. INTRODUCTION

All the Ce^{3+} activated phosphors with the exception of YAG show the maximum of their emission in the UV or blue region ($\lesssim 410$ nm). The emission is ascribed to the $5d - 4f$ transition in the Ce^{3+} ion. The decay time is found to be shorter than 100 ns [1]. Ropp [2] summarized the previous results and described the properties of the Ce^{3+} activated rare earth phosphates. Finally, Brill et al. [3] summarized and determined the decay time, efficiencies and spectral energy distribution of a number of these materials.

The emission from YAG : Ce^{3+} under cathode-ray excitation lies, however, almost entirely in the visible region of light with a broad band peaked at 550 nm [4]. UV excitation evokes the same emission and other two peaked at 340 and 360 nm, respectively. This emission has a double character due to the splitting of the ground state as in the case of other Ce^{3+} activated phosphors [3]. The most intensive 550 nm emission band shows no double structure. YAG : Ce^{3+} is, therefore, an exceptional Ce^{3+} doped phosphor.

The efficiency of all the phosphors depends on several factors. YPO_4 e.g. can be sensitized by the incorporation of Th^{4+} ions [5]. The aim of this paper is to describe some factors influencing the efficiency of the YAG : Ce^{3+} phosphors.

2. EXPERIMENTAL

The samples with the general formula $Y_{3-x}Ce_xAl_5O_{12}$ ($x = 0.010; 0.015; 0.030$) undoped or doped with 5 ppm of either Fe, Pt or Ir, respectively, were prepared from yttrium and cerium oxalates and hydrated alumina containing 5×10^{-4} wt %

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of cationic impurities at most. The concentration of impurities was determined by means of a ZEISS LMA-10 laser-microspectralanalyser (iron group and alkali-earth ions) [6] and by means of luminescence analysis using X-ray excitation (rare earth ions) [7]. The concentration of Ce^{3+} was determined by chemical analysis after dissolving of the crystals.

Two different techniques were used to prepare the phosphors. Polycrystalline and single-crystalline samples were obtained, respectively.

a) Preparation of polycrystalline phosphors

The stoichiometric $((Y + Ce) : Al = 3 : 5)$ mixture of raw materials was fired in air (to avoid carbon compounds) at 1500 °C for 5 hours using high purity alumina crucibles and the polycrystalline sintrates obtained were powdered. A part of the sintrates was further fired in H_2 or in 98% $Ar + 2\%\,H_2$, eventually in air again at 1500 °C and then powdered. Firing was performed in high alumina crucibles. Hydrogen treatment was performed alternatively in the closed molybdenum crucibles using $\sim 10^{-3}$ vol % $H_2O_{(g)}$. A greater H_2O content causes the samples were covered by dark layer. The samples fired in N_2 at the same temperature [4] showed the same properties as the samples fired in air.

Another part of the sintrates was melted for 5 min either in Mo crucibles using 98% $Ar + 2\%\,H_2$ atmosphere and powered in a high purity alumina ball mill. Powdered melts were fired in air, and subjected eventually to the hydrogen treatment as the initial sintrates.

b) Preparation of the single crystal phosphors

YAG :.Ce^{3+} single crystals were investigated. They were pulled by Czochralski method using the molybdenum crucible and 98% $Ar + 2\%\,H_2$ protective atmosphere [8]. A decrease of $Y_2O_3 : Al_2O_3$ ratio in the melt during the growth was observed and evaporated $YAlO_3$ was found on the cold part of the furnace. The crystals started from the stoichiometric $((Y + Ce) : Al = 3 : 5)$ melt showed anomalous bluish-green colour before annealing and, even after annealing in air, very poor luminescence intensity due to the transitive colour centre formation (Fig. 4, Curve 4). During hydrogen treatment light scattering particles were formed in crystals. These crystals were not investigated further. On the other hand the crystals grown from the melt containing $(Y + Ce) : Al$ in the ratio of $3.03 - 3.05 : 5$ showed a slight greyish appearance and decreased luminescence intensity but after annealing in air this colour converts to pure yellow and they showed luminescence intensity comparable with those of sintrates. Hydrogen annealing up to 1600 °C causes no decomposition of the crystals. The crystals were started with conical phase interface to avoid rough structural defects (blocks). After about 15 mm of pulling, the conical interface was converted to the flat one to reach uniform Ce^{3+} concentration in the cross-section of the crystal [8]. Distribution coefficient of Ce^{3+} between the crystal and the melt

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was stated as $C_{(s)} : C_{(I)} = 0.124$. The crystals contained approximately 5×10^{-4} wt % Mo. Using $5 \times 10^{-2} - 1 \times 10^{-1}$ vol. % H_2O in the protective atmosphere, the concentration of the Mo in the crystal increases up to $0.01 - 0.02$ wt %. More increased H_2O content in the atmosphere causes the quality of the crystals to rapidly decrease (light scattering particles, blocks). Plates of 19.5 mm in diameter and 1 mm in thickness were machined from the crystals. A part of the single crystals was powered in a high purity alumina ball mill. The powdered crystals were fired in the same way as the sintrates.

The cathode-ray efficiency measurement of the phosphors was accomplished by means of a modified electron microscope. Herewith the powders prepared either from the sintrates and melts or from the single crystals were distributed by sieve classification and the fraction of $1 - 3$ µm was deposited on a polymethylacrylate desk substrate by the sedimentation technique in amylacetate without further binder. The phosphor layer of 6 mg/cm² in surface density was covered with an organic film and then coated with an aluminium film. The single crystal plates were oneside coated before measurement with aluminium only.

Optical absorption spectra were measured on the plates of 1 mm in thickness using a Unicam SP 700 Spectrophotometer. Transient colour changes were measured using an optical excitation because cathode rays penetrate in a thin surface layer only. Optical excitation of the samples of 3 mm in diameter and 8 mm in length was performed in an elliptical Al coated cylinder reflector with a straight xenon flashlamp which emitted an approximatively rectangular light pulse of 0.7 ms duration and of 0.1 kJ energy. The probe light from another xenon lamp is a pulse of about 0.01 ms duration. This lamp is triggered $0 - 2000$ ms after ignition of the exciting lamp. Transmitted light passing through Zeiss three-prism monochromator enters photomultipliers detecting its intensity between $500 - 1100$ nm. The wavelengths below 500 nm cannot be measured because of strong absorption of Ce^{3+} ions in this region (Fig. 3).

The step of 10 nm between neighbouring measurements was used. The intensity of the transmitted light was measured as a height of the respective pulse on the screen of the osciloscope triggered simultaneously with the probe light emitting lamp.

3. RESULTS

Preliminary experiments showed that the maximum efficiency had been achieved with samples having the formula $Y_{3-x}Ce_xAl_5O_{12}$ where $x \doteq 0.015$. A survey of the results obtained with the samples of this cerium concentration is given in Fig. 1.

Low efficiencies were obtained in the cases with materials doped with Fe, Ir or Pt ions, respectively.

Important results were found using Mo-doped samples where the crystal plates fired in oxygen and, afterwards, in wet hydrogen in molybdenum crucible — they were the best of all the samples.
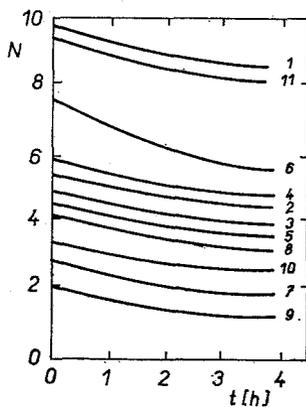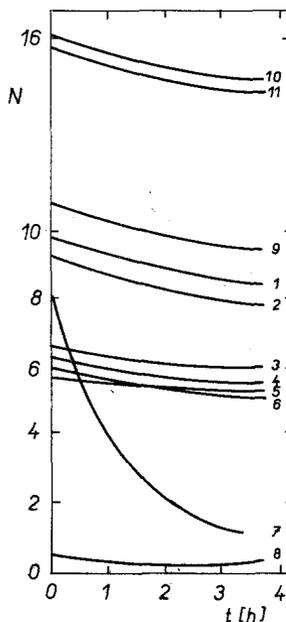
Fig. 1.

Fig. 2.

Fig. 1. The comparison of the luminescence output (N) — in arbitrary units — for different YAG : : Ce^{3+} samples. Incident electron beam $E = 10$ keV, $J = 4 \times 10^{-8}$ A cm^{-2}; electron beam diameter 3 mm. 1 — single crystal (5 × 10^{-4} wt % Mo) fired for 5 hours at 1500 °C in air and then powdered. 2 — sample 1 fired for 50 hours at 1500 °C in air. 3 — sample 2 fired for 5 hours at 1500 °C in H$_2$. 4 — powdered single crystal (untreated) or the sintrate melted in Mo crucible and powdered. 5 — sample prepared by sintering at 1500 °C in air. 6 — sample 5 fired for 5 hours in 98% Ar + 2% H$_2$, afterwards fired for 1 hour at 1400 °C in air. 7 — sample 5 doped with 5 ppm Fe ions. 8 — sample 5 doped with 5 ppm Ir ions. 9 — sample 5 doped with 5 ppm Pt ions. 10 — melted in Ir crucible and powdered. 11 — melted in Mo crucible, fired for 5 hours at 1500 °C in air and then powdered.

Fig. 2. The comparison of the luminescence output (N) — in arbitrary units — for different samples prepared from the YAG : Ce^{3+} single crystal with other Ce^{3+} activated phosphors. Experimental conditions see Fig. 1. 1 — single crystal fired for 5 hours at 1500 °C in air, afterwards powdered (see Fig. 1, sample 1). 2 — single crystal (5 × 10^{-4} wt. % Mo) plate fired for 5 hours at 1500 °C in air; one plane polished, the matted one towards the photomultiplier. 3 — plate as in 2, both planes polished, 4 — Y$_2$Si$_2$O$_7$: Ce^{3+} powdered sintrate. 5 — Ca$_2$Al$_2$SiO$_7$: : Ce^{3+} powdered sintrate (p. 16). 6 — scintilator for SEM JEOL. 7 — plastic scintilator for SEM JEOL. 8 — single crystal containing 2 × 10^{-2} wt. % Mo machined as sample 2. 9 — as the sample 8 fired 5 hours at 1500 °C in wet hydrogen alumina crucible. 10 — as the sample 9 but molybdenum crucible is used. 11 — treated as the sample 10, but the crystal containing 5 × 10^{-4} wt. % Mo is used.
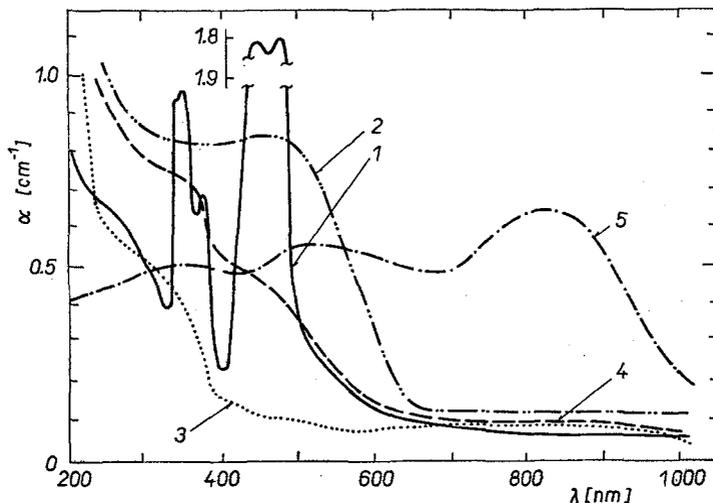
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Fig. 3. Stable absorption spectra of YAG crystals. 1 — doped with Ce ($Y_{2\cdot99}Ce_{0\cdot01}Al_5O_{12}$) after treatment in air or followed by treatment in hydrogen. 2 — doped with 2×10^{-2} wt. % Mo only after treatment in air and irradiated. 3 — undoped, grown from the melt where Y : Al > 3 : 5 cooled by the ratio of $50\,°C\,h^{-1}$. 4 — as the sample 3 cooled by the ratio of $200\,°C\,h^{-1}$ 5 — undoped grown from the melt where Y : Al > 3 : 5.

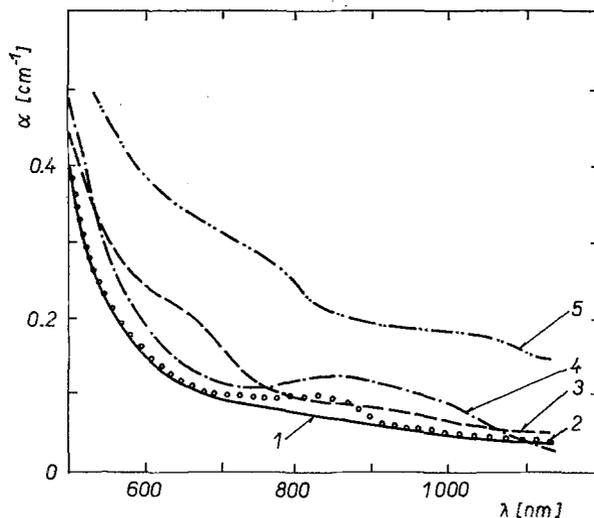Fig. 4. Radiation induced absorption spectra of YAG : Ce on (Y + Ce) : Al ratio. 1 — (Y + Ce) : : Al > 3 : 5 after treatment in air (1500 °C, 5 hours). 2 — (Y + Ce) : Al > 3 : 5 containing 2×10^{-2} wt. % Mo after treatment in air, followed by treatment in hydrogen (1500 °C, 5 hours). 3 — (Y + Ce) : Al > 3 : 5 cooled in the 98% Ar + 2% H_2 by the ratio of $50\,°C\,h^{-1}$, flashed and measured immediately after flashing ($\tau \approx$ 1200 ms). 4 — (Y + Ce) : Al > 3 : 5 treated in air (1500 °C, 5 hours) flashed and measured immediately after flashing ($\tau \approx$ 0·3 ms). 5 — (Y + Ce) : Al > 3 : 5 containing 5×10^{-3} wt. % Mg treated in air (50 h 1500 °C) flashed and measured ($\tau \approx \infty$).

On the other hand all the samples where irradiation or growth induced coloration were found, showed low luminescence intensity (Fig. 4), [11].

The mentioned phosphors can be used with advantage as the scintilators for detection of electron irradiation, e.g. in a scanning electron microscope. Here the YAG : Ce^{3+} single crystal can be used in the form of a plate of $0\cdot5-1\cdot0$ mm in thickness. The surface of the single crystal plate can be finished in various ways. The highest efficiency of the luminescent-optical system achieved with samples first annealed in air and polished on the side of incident electron beam and matted on the side adjacent to the light pipe, particularly after thermal treatment in molybdenum crucible under slightly wet hydrogen atmosphere where the transfer of molybdenum as a compound from the crucible into surface layer of the crystal is possible. It was also semi-quantitatively confirmed by the laser spectral analysis of the surface layer.

The comparison of these results and the comparison of samples prepared from YAG : Ce^{3+} and other Ce^{3+} activated phosphors [3] is given in Fig. 2.

4. CONCLUSIONS

The obtained results can be summarized as follows: The presence of Fe, Ir and Pt ions, respectively, causes luminescence quenching of Ce^{3+} ions. Such a result is not suprising with respect to a similar action of Fe ions e.g. in the ruby laser [9].

Treatment in the 98% Ar + 2% H_2 atmosphere (e.g. during the crystal growth) brings about a deep reduction (or excess of the metallic ions) of the basic material without its decomposition. Growing the YAG crystals with an excess of Al_2O_3 in the melt (in the above mentioned atmosphere) these have the same absorption spectrum (blue colour) as YAG treated in aluminium vapour [10]. Moreover, further stable colour centres (wide absorption between $280-550$ nm) are formed even in the case of the excess of Y_2O_3 in the melt [11]. Colour centres cause luminescence quenching of YAG : Ce^{3+} as it is known from the crystalline materials [9, 12]. Stable colour centre can be annealed by a thermal treatment in an oxidizing atmosphere but the crystals containing more Al^{3+} showed irradiation induced transient colour centre of the same absorption as those observed in unannealed crystals. The samples having no superfluous Al^{3+} showed after prolonged oxygen treatment a slightly enlarged stable colouration between $280-550$ nm. The decrease of the efficiency after prolonged annealing (particularly in the powder) in oxidizing conditions is connected with this absorption. It may be explained by the presence of small amounts of iron group ions, Mg or Mo, respectively, which in fully oxidized YAG make presence of the stable radiation induced colour centre possible [13] (The measurement with the crystal doped with 5×10^{-3} wt % Mg confirms this explanation.).

Following hydrogen treatment suppresses the formation of the colour centre (no changes in absorption). The samples containing more Mo ions in the reduced, i.e.

probable 3+ state [14] amplifies substantially the luminescence output of Ce^{3+} ions. This phenomenon cannot be explained at present but the absorption spectrum of the samples containing both cerium and molybdenum ions indicates the possibility of their interaction. The treatment of the crystal plates in wet hydrogen using a closed molybdenum crucible causes the concentration of molybdenum ions in the surface layer to be increased without destruction of the material. That is why these samples showed at least the same luminescence output in the condition of CR excitation as the latest Ce^{3+} doped phosphors [15] but the exceptionally short decay time of YAG : Ce is retained.

The way of finishing the plates of the YAG : Ce^{3+} single crystal influenced substantially their optical properties. The polishing or matting of individual surfaces of the plate influences the output of the emitted light into the light-pipe placed between the single crystal plate and the photomultiplier, because the polished surface reflects a greater portion of light back into the sample than the matted one.

5. SUMMARY

Luminescence intensity of YAG : Ce^{3+} under cathode ray excitation depends on the presence of dopants and surface quality. Iron, iridium and platinum ions cause luminescence quenching, whereas the purest material prepared in 98% Ar + 2% H_2 atmosphere showed very strong luminescence efficiency particularly after weak thermal treatment in oxidizing atmosphere. Single crystals seems to be better than the material prepared by sintering of the simple compounds because it showed a minimal temporal decay.

Single crystal plates containing an increased Mo content on the side of impinging electron beam seems to be the best of all hitherto known Ce^{3+} activated phosphors.

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