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Cathodoluminescent Efficiency of $Y_3Al_5O_{12}$ and $YAlO_3$ Single Crystals in Dependence on Ce^{3+} and Other Dopants Concentration

The content of Ce^{3+} ions in the investigated single crystals grown under reducing conditions is limited by a low value of the distribution coefficient. This distribution coefficient decreases sharply with increasing concentration of Ce^{3+} ions in a melt. Cathodoluminescent efficiency rises with increasing Ce^{3+} concentration up to a certain state of saturation. At higher concentrations of Ce^{3+} ions emission from activator centres is dominant, while at lower concentrations defect centres play an important part. Iron acts as a strong quenching centre, especially in the $YAlO_3$ lattice. Nd, Ir, Fe, Ti, Cr centres exhibit a high quenching effect, too. A trace amount of Mo enhances cathodoluminescent efficiency.

Der Gehalt an Ce^{3+}-Ionen in den untersuchten Einkristallen wird unter Reduktionsbedingungen des Kristallwachstums durch den niedrigen Wert des Verteilungskoeffizienten begrenzt. Der Verteilungskoeffizient vermindert sich stark mit zunehmender Konzentration der Ce^{3+} Ionen in der Schmelze. Die Kathodolumineszenzausbeute wächst mit steigender Konzentration der Ce^{3+} Ionen bis zu einem bestimmten Sättigungszustand. Bei höheren Konzentrationen von Ce^{3+} Ionen zeigt sich die Emission aus Aktivatorzentren dominant, während bei niedrigen Konzentrationen Defektzentren wirksam werden. Eisen stellt ein starkes Löschzentrum dar, hauptsächlich im $YAlO_3$-Gitter. Hohe Löschwirkung zeigen auch die Nd, Ir, Fe, Ti, Cr Zentren. Eine Spurmenge von Mo trägt zur Erhöhung der Kathodolumineszenzausbeute bei.

1. Introduction

Yttrium aluminium garnet $Y_3Al_5O_{12}$ (YAG) and yttrium aluminium perovskite $YAlO_3$ (YAP) possess suitable host lattices for activation by elements of rare earths. Among these elements trivalent cerium plays the most important part. It has a very short decay time of liminescence and this property is inevitable for applications in which a fast course of luminescent process is required, as e.g. in scanning electron microscopy for signal electron detection. Single crystals of YAG:Ce^{3+} and YAP: Ce^{3+} are therefore used as efficient and fast scintillators and screens in electron optical devices (Autrata et al. 1978, 1983).

Their properties, above all quantum efficiency, decay time of luminescence, emitted light spectrum, lifetime are dependent not only on the kind of activator used, but also on its concentration in the host lattice and on eventual presence of some elements nominally undoped but acting as impurity dopants. Technological conditions of preparation of the described single crystals as well as additional temperature treatment of as grown crystals in different atmosphere affect their final properties, too.

The influence of cerium on luminescent properties of YAG and YAP single crystals was investigated by ROBBINS et al. Technological conditions of single crystal growth presented by these authors are different from those used at growing the single crystals in our laboratory.

2. Experimental

YAG and YAP single crystals were grown by the Czochralski method using a molybden crucible in a reducing atmosphere of 98% Ar and 2% H_2. By growing the single crystals from a melt comprising ions of yttrium, cerium and aluminium in the atomic ratio (Y + Ce): Al = 3.0 ± 0.2:5 in an atmosphere containing argon and hydrogen the concentration of impurity dopants, such as manganese, iron, cobalt, nickel, chromium, iridium, is considerably decreased. Otherwise these dopants quench very effectively luminescence of cerous ions. Besides, a single crystal can contain an excess of Y^{3+} and Al^{3+} ions which can give rise of formation of colour centres in the grown crystals. These centres also quench the luminescence and consequently decrease the resulting efficiency because of their intensive absorption in the luminescence region of cerous ions. By heating a single crystal in an atmosphere containing hydrogen or in vacuum the excess amount of aluminium and yttrium is removed. As a result the so-called "grow" colour centres disappear and ions of trivalent cerium fill the dodecahedral positions. In spite of that, vacancies left after oxygen treatment do still exist in the crystal which may be the possible acceptors of electrons when the specimen is induced by an electron beam. This leads to prolongation of the decay time of luminescence. For this reason the single crystals are subsequently heated at a lower temperature in an atmosphere containing free oxygen. At this temperature the content of oxygen is filled up and no cation vacancies arise. The diffusion of cerous ions into octahedral positions during which ceric ions are supposed to arise is faint under these conditions. Ceric ions similarly as ions of most transition elements quench luminescence of cerous ions. Therefore their presence is undesirable. Other conditions of crystal growth were described earlier (KVAPIL et al. 1981).

Cathodoluminescent efficiency measurements were made in an adapted electron microscope in which the beam of primary electrons was used for excitation of luminescence in the YAG and YAP single-crystal plates. Electrons were incident on the crystal plate surface with 10 keV energy and current density of $4 \cdot 10^{-8}$ A/cm^2. The detection of luminescence was effected by means of photomultiplier 65 PK 415 (Tesla). At measurements of emission spectra an appropriately modulated light signal was detected after passage through the mirror monochromator SPM 1 (VEB Carl Zeiss Jena) with the help of photomultiplier 9558 B (EMI) and a lock-in nanovoltmeter 232 B (Unipan). Concentration of Ce^{3+} ions and other impurity dopants was detected by the method of atomic absorption spectrophotometry and neutron activation analysis.

Cathodoluminescence efficiency was measured in the dependence on the concentration of trivalent cerium using 0.5 mm thick discs cut from an as grown crystal. These discs were then heated identically at a temperature of 1500—1700 °C in oxygen and thereafter hydrogene atmosphere. Only those specimens were chosen for measurements showing concentration of impurity dopants less than $1 \cdot 10^{-4}$ wt.%. In such a way unfavourable effect of other quenching centres on cathodoluminescent efficiency was eliminated and the influence of concentration of Ce^{3+} centres could be studied with good accuracy.

Melts of different Ce^{3+} concentration were prepared. About 50% of the melt were converted into single crystals. As the concentration of Ce^{3+} ions in the lower part of the crystal was 2.5 times higher than that in the upper part under the seed crystal the specimens for measurements were taken only from that part of the crystal localized at one third from the crystal top. The concentration of Ce^{3+} ions was determined on the same specimen on which cathodoluminescent properties were measured before.

3. Results

Table 1 gives values of the distribution coefficient of Ce^{3+} ions between the melt and the single crystal $Y_3Al_5O_{12}$. The Ce^{3+} concentrations were determined by atomic absorption spectroscopic methods and the additional testing was made by neutron activation analysis.

Table 1
Distributions coefficients for Ce^{3+} ions in YAG single crystals

melt composition			crystal composition	distribution coefficient
CeO_2 (g)	melt (g)	at.% Ce^{3+}	at.% Ce^{3+}	k
0.02	400	0.0057	0.0056	0.9756
0.03	550	0.0062	0.0056	0.9009
0.5	400	0.1437	0.0070	0.0490
3.0	400	0.8625	0.0113	0.0130
7.0	400	2.0120	0.0197	0.0098
12.0	400	3.4500	0.0283	0.0082

In the given range of concentration the distibution coefficient value changes within the limit of two orders. For the highest concentration of Ce^{3+} 3.4 at.% (related to Y^{3+}) in the melt this value is 0.008 and for the lowest concentrations of Ce^{3+} $5.7 \cdot 10^{-3}$ at.% in the melt it corresponds to 0.97. The value of the distribution coefficient is by one to two orders lower than that quoted by Robbins et al. The reason may consist in different conditions of crystal technology. The low value of our distribution coefficient can be ascribed to reducing conditions used for growth of our crystals under which trivalent cerium only unwillingly incorporates into the lattice of garnet or perovskite. The oxidizing conditions used by Robbins et al. enhance the solubility of cerium ions but give probably rise to Ce^{4+} ions quenching luminescence.

The influence of Ce^{3+} concentration on the cathodoluminescent efficiency was investigated as "relative cathodoluminescent intensity" (RCLI) which means the luminescent yield corresponding to the characteristic spectrum of Ce^{3+} activator (565 nm for YAG, 378 nm for YAP) excited after incidence of electrons on the specimen, detected through a monochromator by a photomultiplier with a photocathode S 20 corrected for its maximum spectral sensitivity.

Figure 1 shows RCLI for YAG and YAP as a function of Ce^{3+} concentration. Points on the curves correspond to specimens in which concentration of impurity dopants (Nd, Mo, Fe, Ir, Pt, Ti, Cr) was lower than 10^{-4} wt.%. All YAG specimens given in Figure 1 were of "as grown" type exclusively, no additional treatment was used. Only YAP specimens were annealed in the reducing atmosphere, all under the same conditions. It follows from the curves in Figure 1 that RCLI rises with increasing Ce^{3+} concentration up to a certain state of saturation. With YAG the state of saturation of RCLI is reached at concentrations approaching $1 \cdot 10^{-1}$ at.% and in the case of YAP at concentrations somewhat higher. Figure 1 also shows a curve of RCLI from defect centres of YAG emitting in the wavelength region of 400 nm. The share of the defect centres in emission is greater at low concentrations of cerium. The presence of defect centres affects both RCLI of the characteristic emission band (565 nm) and the decay of cathodoluminescence. The higher the concentration of defects, the steeper decreases the intensity of the characteristic cathodoluminescence with decreasing concentration of Ce^{3+} ions. The excitation energy is distributed

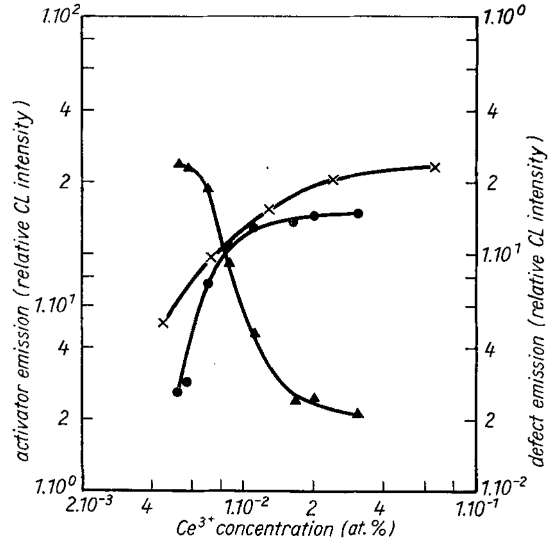

Fig. 1. Relative cathodoluminescent intensity of emission from activator and defect centres as a function of activator concentration. ● activator emission of YAG : Ce^{3+}, × activator emission of YAP : Ce^{3+}, ▲ defect emission of YAG : Ce^{3+}

between the defect and activator Ce^{3+} centres. The activator centres are dominating at a con centration higher than $1 \cdot 10^{-2}$ at.%. The presence of the defect centres is also proved by measurements of the time dependence of luminescence. This will be discussed in the next paper.

The characteristic bands of 565 nm for YAG and 380 nm for YAP do not change their positions if Ce^{3+} concentration changes. Their intensity decreases either with the decreasing concentration of Ce^{3+} or with the increasing content of impurity dopants

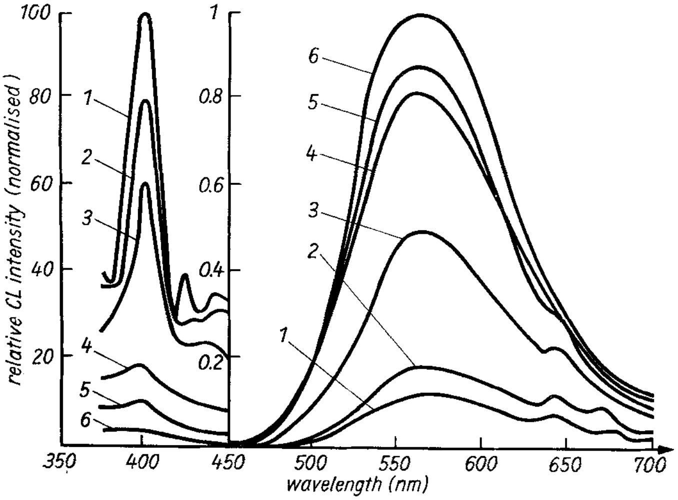

Fig. 2. Cathodoluminescent spectra of YAG single crystals for different Ce^{3+} ions concentrations. 1 — Ce^{3+} concentration $5.6 \cdot 10^{-3}$ at.%, 2 — Ce^{3+} concentration $6.2 \cdot 10^{-3}$ at.%, 3 — Ce^{3+} concentration $7.0 \cdot 10^{-3}$ at.%, 4 — Ce^{3+} concentration $1.13 \cdot 10^{-2}$ at.%, 5 — Ce^{3+} concentration $1.97 \cdot 10^{-2}$ at.%, 6 — Ce^{3+} concentration $2.83 \cdot 10^{-2}$ at.%

and defects. The emission spectrum of YAG with different concentrations of Ce^{3+} is shown in Figure 2. The curve of intensity of the characteristic emission is normalized with respect to the maximum and all values are corrected for spectral sensitivity of the photomultiplier. The intensity of non-characteristic emission corresponding to emission from the defect or impurity centres expressed more in detail amounts to the hundredth multiple of the normalized value. The curve corresponding to very low concentration of Ce^{3+} ($5.6 \cdot 10^{-3}$ at.%) resembles the curve of nominally undoped YAG. The maxima ocurring in the characteristic region of the spectrum correspond in the case of these specimens to some impurity dopants present in a trace amount — especially to neodym. Specimens with the lowest RCLI of the characteristic band corresponding to the lowest concentration of Ce^{3+} have their most pronounced maxima in the UV region at 400 nm wavelength. On the contrary, specimens with a high concentration of Ce^{3+} show the highest RCLI in the characteristic region of the spectrum and the lowest RCLI in the UV region of the spectrum. This gives evidence of the share of defect and activator centres in the energy transfer. The negative effect of the defect centres both in connection with RCLI and with the decay of luminescence is a result of undesirable transfer of energy to the activator and the probability of non-radiative recombination in these centres.

RCLI is influenced not only by defect centres but also by the presence of different nominally undoped impurities. Their concentration depends not only on the purity of the initial raw material but also on the kind and purity of crucibles, purity of the protecting atmosphere and the furnace itself. We have published earlier (Kvapil et al. 1980) that irridium and platinum — metals very often used for growing single crystals — are the most effective quenching impurities. In the present paper we study influence of some other elements used besides the constant concentration of Ce^{3+} as additional impurity dopants in the crystal.

The unfavourable influence of iron becomes evident in the case of the perovskite structure which in comparison with the garnet structure accepts impurity ions more easily and forms colour centres. Figure 3 shows that the content of iron exerts no influence on the shift of the spectral band of the characteristic emission of YAP: Ce^{3+}. However, RCLI of this band decreases sharply with the increasing amount of iron. The initial material used for crystal growth often contains about $1 \cdot 10^{-4}$ wt.% of

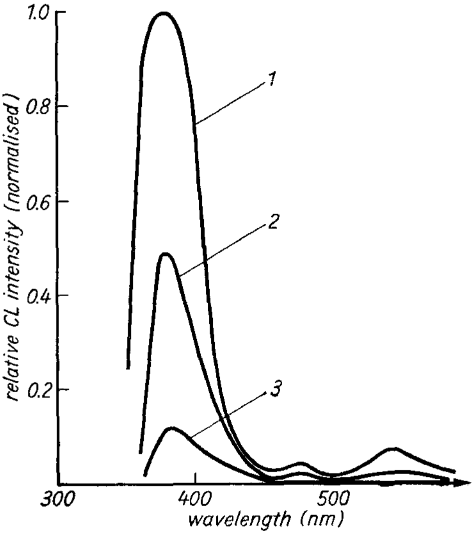

Fig. 3. Cathodoluminescent spectra of YAP: Ce^{3+} in dependence on Fe ions concentration. 1 — Fe concentration $1 \cdot 10^{-4}$ wt. %, 2 — Fe concentration $6 \cdot 10^{-4}$ wt.%, 3 — Fe concentration $1 \cdot 10^{-3}$ wt.%

iron, no additional iron can be built into the crystal from the material of the crucible of furnace. Long-time melting (40—50 h) of the raw material in a protective atmosphere decreases Fe concentration to a value undetectable by absorption spectroscopy or neutron activation analysis.

It can be seen from Table 2 that the RCLI value decreases with the increasing content of iron in the YAP: Ce^{3+} single crystal. The maximum value of RCLI is related to the YAP: Ce^{3+} single crystal containing a trace amount of molybden. It has been proved that molybden has a favourable influence on RCLI of the YAG: Ce^{3+} single crystal, too, as evident from the table.

Table 2
Influence of some secondary impurity dopants on the cathodoluminescent intensity

lattice	impurity dopant	wt.%	RCLI %
YAP: Ce^{3+}	Mo	$1 \cdot 10^{-4}$	100
	Fe	$1 \cdot 10^{-4}$	82
	Fe	$6 \cdot 10^{-4}$	38
	Fe	$1 \cdot 10^{-3}$	8
YAG: Ce^{3+}	Mo	$4 \cdot 10^{-4}$	85
	Mo	$2 \cdot 10^{-4}$	81
	Cr	$1 \cdot 10^{-4}$	61
	Ti	$2 \cdot 10^{-4}$	59
	Ir	$8 \cdot 10^{-4}$	42
	Nd	$2 \cdot 10^{-4}$	38

On the contrary, RCLI is affected very unfavourably by neodymium which may come from the original raw material. In the YAG: Ce^{3+} single crystal neodymium forms centres with a great probability of non-radiative recombination. A part of energy can be transferred from the neodymium centres to the activator by resonance and in this way the decay time of luminescence is prolonged. Unlike other investigated impurity dopants neodymium participates in forming maxima in the cathodoluminescent spectrum. Other investigated impurity dopants such as Cr, Ti, Fe, Ir do not probably take part in the transfer of the excitation energy to the activator and also are not effective in the cathodoluminescent spectrum. However, they act as centres of nonradiative recombination and lower therefore the efficiency of the transfer of the excitation energy through the basic lattice. As can be seen in Table 2 even their low concentration can essentially affect RCLI.

4. Conclusions

Ce^{3+} ions are incorporated into the lattice of YAG or YAP very uneasily as can be proved by the low distribution coefficient and its decreasing value with increasing concentration of Ce^{3+} ions in the melt. This is caused by reducing conditions of crystal growing under which Ce^{4+} ions formation is considerably suppressed. Ce^{4+} ions are incorporated into the crystal lattice with a higher distribution coefficient but do not contribute to luminescent emission. With the increase of Ce^{3+} concentration in the single crystal the cathodoluminescent efficiency rises to the state of saturation. If the concentration of Ce^{3+} ions in the YAG single crystal is increased over the limit $2 \cdot 10^{-2}$ at.% and the distribution coefficient is smaller than 0.009, cathodoluminescence efficiency increases only negligibly. The behaviour of the YAP single crystal is similar. In the region of the given concentration cathodoluminescent emission is excited dominantly from activator centres, while at lower concentrations defect centres play an important part.

Iron acts as a strong excitation centre, especially in the YAP single crystal lattice. The increasing content of iron brings about a steep decrease of cathodoluminescent efficiency. The characteristic emission band does not change its position. Nd, Ir, Fe, Ti and Cr centres belong to impurity centres with a high quenching effect. A trace amount of molybden enhances cathodoluminescent efficiency.

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