Spectroscopy and scintillation properties of cerium doped YAlO$_3$ single crystals

Spectroscopy and scintillation properties of cerium doped YAlO₃ single crystals

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Abstract. A study of the spectroscopic and scintillation properties of Ce doped YAlO₃ single crystals is presented. The relation between the method of crystal growth, in vacuum or by the Czochralski method, and the above properties was studied specifically. Vacuum grown crystals show a scintillation light yield of about 14 000 photons per megaelectronvolt of absorbed x-ray energy. It is concluded that cation vacancies present in the Czochralski grown crystals cause a decrease of the light yield. The influence of colour centres such as F and F⁻ centres on the spectroscopic and scintillation properties will be discussed.

1. Introduction

Scintillators based on single crystals of yttrium aluminium perovskite (YAlO₃, YAP) doped with cerium ions are increasingly used in the detection of ionizing radiation [1–3]. However, the spectroscopic properties as well as their relation to scintillation parameters are still the subject of discussion in the literature. Starting from the first work by Weber [4], the main characteristics of YAP:Ce crystals related to the trivalent Ce^{3+} ions were established [5–8]. The authors of [5] showed that the scintillation efficiency of YAP:Ce single crystals depends strongly on the method of crystal growth. Moreover, the decay kinetics of YAP:Ce scintillation pulses is non-elementary [6], and the contribution of fast and slow components to the scintillation kinetics is largely determined by the method of crystal growth and subsequent heat treatments.

The present paper deals with the investigation of the relation between spectroscopic and scintillation properties of Ce doped YAP single crystals. Since the scintillation effect in YAP:Ce single crystals is determined by the 5d–4f interconfigurational luminescence of Ce^{3+} ions, we focus our attention on the excitation and quenching mechanisms of Ce^{3+} luminescence. After the effect of unintentional impurities on the 5d–4f luminescence, one should consider the following causes of luminescence quenching: (i) excited state absorption in Ce^{3+} ions; (ii) concentration quenching; and (iii) quenching due to energy exchange with colour centres. The first cause is effective only at high photon excitation intensities, which is not realized except in laser physics. In the case of scintillators it does not manifest itself. The second is not important either since no concentration quenching was observed at the optimal Ce concentration [2] of ~ 0.2 mass%. Considering the third cause, one should realize that colour centres in crystals may arise from both intrinsic point defects of the host matrix and substitutional defects introduced as a results of incorporation of Ce^{2+} and Ce^{4+} ions into the matrix during crystal growth. Therefore, to clarify the role played by different

types of defect in the quenching of 5d–4f luminescence, we investigated both Ce doped and undoped YAP crystals. The investigation of undoped crystals made it possible to identify colour centres related to intrinsic point defects.

2. Experimental details

Two types of crystals were investigated. We prepared undoped and Ce doped samples grown by the method of horizontally oriented crystallization in molybdenum containers in vacuum, and by the Czochralski method in iridium crucibles in an inert (argon) gas atmosphere. The Ce concentration in the samples was close to the optimal value [2].

A Beckman UV 5760 and a Specord M40 were employed to measure optical absorption spectra. An SDL2 luminescent spectrometer was used to measure luminescence and excitation spectra. The crystals were excited with photons using a wavelength resolution of 1–10 nm. A PRA-3000 spectrofluorometer was used to measure luminescence kinetics. An ARC (Acton Research Corporation) vacuum monochromator (model VM-502) was employed to measure luminescence spectra of crystals under excitation with x-rays from an x-ray tube with a copper anode and operated at 35 kV, using a wavelength resolution of 4 nm. A Philips XP2020Q photomultiplier tube was used to detect scintillation light. The decay spectra of 662 keV γ-ray excited scintillation pulses from the crystals were determined by the single-photon counting technique described in [9].

3. Results and discussion

3.1. Spectroscopy

As a rule, colour centres in undoped crystals of oxide compounds are caused by lattice point defects and are related to cation (V_c) and oxygen (anion) V_O vacancies.

Spectroscopic characteristics of colour centres in non-activated single crystals [11–13] and those activated by Nd^{3+} ions have been investigated in [14] and [15]. It has been established that absorption bands in YAP crystals at 300 nm, 360 nm, 400 nm, 480 nm, 560 nm, and 630 nm are caused by colour centres. Arsenev *et al* [15] indicate that γ-irradiated YAP:Nd single crystals show luminescences at $\lambda = 500$ and 600 nm, and in [13] this luminescence is attributed to colour centres based on O vacancies. Neither the connection between the growth conditions of single crystals and the presence of these colour centres, nor the role of these centres in the energy transfer from or to other luminescence activating impurities has been studied yet.

It is expected that in the vacuum grown crystals, the F ($=V_O+2e$) and F^+ ($=V_O+e$) centres will dominate, whereas in the Czochralski grown crystals one can observe an increased number of colour centres related to V_c^{2-} ($=V_c+h$), V_c^- ($=V_c+2h$) and so on.

Some spectroscopic properties of undoped crystals are shown in figure 1. In the absorption spectrum of the vacuum grown crystal, an absorption band is observed in the near ultraviolet region at $\nu_1 \simeq 36000$ cm^{-1}. In the Czochralski grown crystals, this absorption band is considerably weaker. These latter crystals have an additional weak absorption band near $\nu_2 \simeq 24400$ cm^{-1}, which is not observed in the vacuum grown crystals. The vacuum grown crystals show in the region between 30000 cm^{-1} and 23000 cm^{-1} an absorption that decreases monotonically without pronounced bands. Excitation in the short-wavelength region produces a luminescence band at $\nu_3 = 16600$ cm^{-1}. Excitation in the long-wavelength region gives rise in addition to ν_3 to $\nu_4 = 15000$ cm^{-1}. Both luminescence

bands are characterized by similar decay kinetics. In the intensity region $I_0 > I > 0.01 I_0$ under photoexcitation, the decay of ν_3 luminescence is bi-exponential with $\tau = 2.4 \pm 0.5$ ns and $\tau = 19.9 \pm 0.5$ ns. ν_4 has decay components with $\tau = 1.3 \pm 0.3$ ns and 16.3 ± 0.5 ns. The origin of the strong absorption in vacuum grown crystals beyond $36\,000$ cm^{-1} was not studied. Since pure YAP crystals are metastable, they are probably stabilized by unintentional impurities or defects, which may be responsible for this strong absorption.
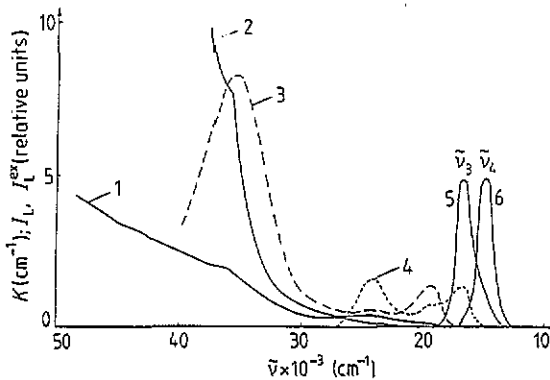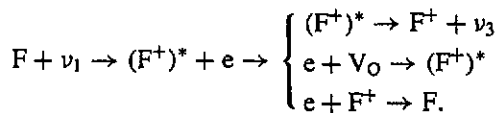

Figure 1. Absorption (K) spectra of undoped YAP single crystals grown by the Czochralski method (1) and by horizontally oriented crystallization in vacuum (2). (3) Luminescence excitation spectrum, I_L^{ex}, of the normalized emission band at $\nu_3 = 16\,600$ cm^{-1} (5) in vacuum grown crystals, and the excitation spectrum (4) of the normalized emission band at $\nu_4 = 15\,000$ cm^{-1} (6) in Czochralski grown crystals. The spectra were recorded at room temperature.

The measurement of the luminescence excitation spectra made it possible to identify additional excitation bands caused by radiative centres. In the visible region, an excitation band at $\nu_5 = 19\,230$ cm^{-1} was recorded for the emission at ν_3. Excitation bands at ν_5 and at $\nu_6 = 16\,260$ cm^{-1} were recorded for the emission band at ν_4. Moreover, under irradiation in the ν_1 excitation band for 1 h, the vacuum grown crystals are coloured and the intensity of the absorption band at ν_1 decreases. Absorption bands at ν_5 and ν_6, which were also present in the excitation spectra, appear upon colouration.

Irradiation in the ν_5 band for 1 h does not change the absorption spectrum. The initial absorption spectrum is restored and the crystals are decolourized (bleached) completely by irradiation in the range $30\,000$–$25\,000$ cm^{-1} over 3 h.

We attribute the emission band at ν_3 to defects that can both preserve and change their charge state, and which are related to O vacancies in the lattice. Such luminescence can arise due to ionization of the F centres by ν_1 excitation:

$$F + \nu_1 \rightarrow (F^+)^* + e \rightarrow \begin{cases} (F^+)^* \rightarrow F^+ + \nu_3 \\ e + V_O \rightarrow (F^+)^* \\ e + F^+ \rightarrow F. \end{cases}$$

It can also arise from ionization of F$^+$ centres under ν_2 excitation:

$$F^+ + \nu_2 \rightarrow F^{2+} + e \rightarrow (F^+)^* \rightarrow F^+ + \nu_3$$
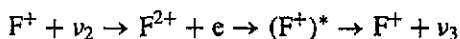
or during direct intrinsic excitation of F$^+$ centres:

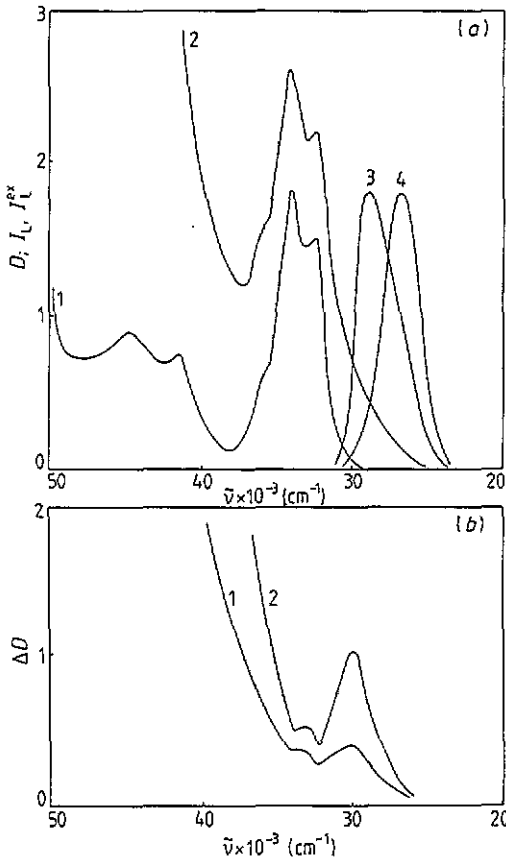$$F^+ + \nu_5 \rightarrow (F^+)^* \rightarrow F^+ + \nu_3.$$
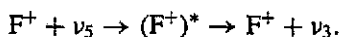
Figure 2. (a) Absorption (D) spectra of YAP: Ce single crystals containing 0.12 mass% Ce (CeO$_2$) grown by the method of horizontally oriented crystallization (1) and the Czochralski method (2). (3) and (4) are the normalized photoexcited ($\nu_{ex} = 33\,300$ cm^{-1}) luminescence (I_L) spectra of the two types of crystal, respectively. (b) Differential absorption (ΔD) spectra of crystals grown by the Czochralski method with a subsequent annealing in vacuum or in an oxidizing atmosphere: (1) the vacuum annealed sample is placed in the reference channel, the crystal as grown is placed in the measurement channel; (2) the crystal as grown is placed in the reference channel, the crystal annealed in air is in the measurement channel. All spectra were measured at room temperature.

Note that the first series of reactions accounts for the photoinduced colouring of the crystals grown in vacuum. Photoionization of F centres is accompanied by an increase of the F$^+$ centre concentration owing to both the photoionization of the F centre and to the trapping of electrons in O vacancies; V$_O$ + e$\rightarrow$ F$^+$. The spectral region 30 000–25 000 cm^{-1} contains the band of F$^+$ centre photoionization. Irradiation in this band causes a bleaching of the samples.

When investigating the nature of the luminescence band at ν_4, it should be noted that it can be excited with the ν_5 band. Apparently, there is a sensitization of the ν_4 emission band by the F$^+$ centres. The fact that the excitation band at ν_2 of the luminescence at ν_4 appears also in the luminescence excitation spectrum of ν_3 can be explained by the formation of the above mentioned F$^+$ centres in the excited state. This process is most likely to proceed via the conduction band, i.e. irradiation in the band $\nu_2 = 24\,400$ cm^{-1} yields photoionization of

colour centres, which causes the luminescence band at ν_4. Thus, the excitation bands at ν_2 and ν_6 can be assigned to the same centre as the one which emits at ν_4.

Since emission ν_4 dominates in the Czochralski grown crystals, it is probably related to the colour centres associated with the cation vacancies. The similarity of the decay kinetics of the ν_3 and ν_4 emission bands as well as their excitation spectra implies that the emitting centres are similar in nature. We propose that the ν_4 emission band is caused by F^+ centres that are located near cation vacancies. This assumption seems to be justified, since undoped crystals may have uncharged associates of type $(V_c^- - F^+)$. Because defect associates are spatially more extended than point defects are, they have probably a greater probability of trapping a free charge carrier. In that case, the charge neutrality can be quickly recovered which may explain the observed photostability of crystals grown in a low-oxidizing atmosphere.

From now on we will refer to the F^+ centres responsible for the ν_3 emission band as F_1^+ and the centres responsible for the ν_4 emission band as F_2^+.

Figure 2(a) presents the spectra of YAP:Ce single crystals grown by different methods. The absorption spectra of both types of crystal contain the known [4] two groups of bands with subbands at $\nu = 35\,714$, $33\,700$, $32\,260$ cm^{-1} and $45\,000$, $41\,450$ cm^{-1}. The two main bands correspond to the interconfigurational transitions in Ce^{3+} ions: $4f^1(^2F_{5/2}) \rightarrow 5d^1(^2T_2)$ and $4f^1(^2F_{5/2}) \rightarrow 5d^1(E)$. Under excitation in these bands, one observes interconfigurational 5d–4f luminescence of Ce^{3+} ions with maximal emission intensity located at ν_{max} in the region $28\,800$–$27\,700$ cm^{-1} depending on the crystal growth method. In doped crystals, Ce^{2+} and Ce^{4+} ions are observed along with Ce^{3+} ions. Their abundance is determined by the gas atmosphere in which the crystals were grown. In the vacuum grown crystals, the Ce^{2+} ions will dominate over the Ce^{4+} ions, while the reverse situation is observed for the Czochralski grown crystals. This is confirmed by the fact that the annealing of vacuum grown crystals carried out in an oxidizing atmosphere ($T = 1200\,°C$, $t = 5$ h) results in an increase by 15–20% of the Ce^{3+} absorption bands. Vacuum annealing of Czochralski grown crystals ($T = 1200\,°C$, $t = 5$ h) also yields increased absorption in these bands, but the increase is much smaller (3–5%).

Czochralski grown crystals exhibit an additional absorption band in the region $31\,000$–$27\,000$ cm^{-1} which causes absorption of the short-wavelength part of the Ce^{3+} emission band. Compared to the vacuum grown crystals, a shift of the emission maximum towards longer wavelengths is effectively observed. The structure of the additional absorption band can be resolved by measuring differential absorption spectra of the Czochralski crystals as grown with Czochralski crystals annealed in vacuum ($T = 1200\,°C$, $t = 10$ h) or in an oxidizing atmosphere ($T = 1200\,°C$, $t = 10$ h).

The differential spectrum, see figure 2(b), shows an absorption band at $\nu_7 = 30\,000$ cm^{-1} and a broad structureless band in the region beyond $35\,000$ cm^{-1}. The absorption intensity of both bands increases as a result of the oxidizing annealing treatment. Since this treatment increases the Ce^{4+} concentration, we propose that the additional absorption band at $30\,000$ cm^{-1} is caused by substitutional defects compensating the extra charge of the Ce^{4+} ions. The defect is probably a cation (Y^{3+}) vacancy with two trapped holes, i.e. a V_c^- which stabilizes the Ce^{4+} ion. Weber [4] and Konstantinov *et al* [10] showed that hole centres in oxide crystals of complex structure, e.g. Y$_3$Al$_5$O$_{12}$, are temperature stable. Furthermore, such centres in oxides are usually characterized by only one absorption band. The nature of the structureless absorption band beyond $36\,000$ cm^{-1} is not known.

Figure 3 shows the energy level diagrams of the colour centres discussed in this work, i.e. F, F_1^+, F_2^+, V_c^-, and the diagram of Ce^{3+} ions. The electronic transitions responsible for the observed excitation, absorption, and emission bands are also shown. Comparing these
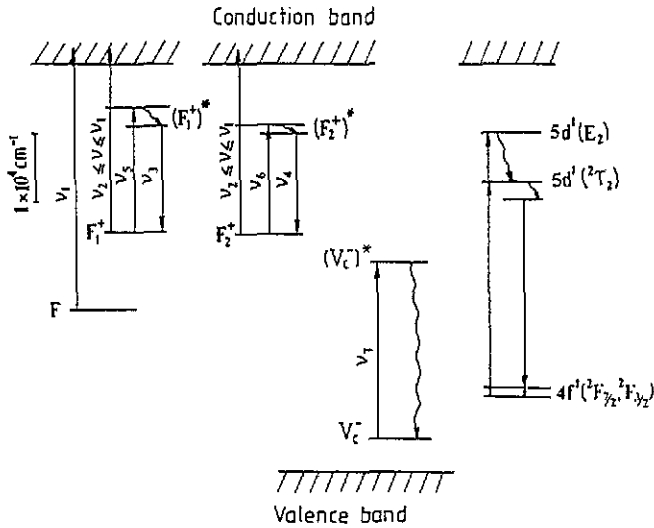
Figure 3. Energy level diagrams of the colour centres and Ce^{3+} ions in YAP crystals.

transitions we envisage several possible quenching mechanisms of Ce^{3+} 5d–4f luminescence. In the vacuum grown crystals with the presence of F and F_1^+ centres, energy exchange resulting in the quenching of Ce^{3+} luminescence intensity may proceed according to the scheme $(Ce^{3+})^* + F_1^+ \rightarrow Ce^{3+} + V_O + e$. This is the case because the Ce^{3+} emission band overlaps with the ν_2 photoionization band of the F_1^+ centre. As will be shown later, this process does not yield a substantial quenching of the Ce^{3+} luminescence and hence a strong decrease of the luminescence efficiency. It may cause a slight change of the scintillation decay kinetics. A similar energy transfer to F_2^+ centres may be expected. In the Czochralski grown crystals, a strong quenching of luminescence and hence a lower light yield compared to vacuum grown crystals should be observed due to the overlap of the 5d–4f luminescence band with the V_c^- absorption line. A change of the decay kinetics of the 5d–4f luminescence may also be expected.

3.2. Scintillation properties

When excitation occurs by the absorption of ionizing radiation (x-rays, γ-quanta, α-particles), the luminescence spectra of the vacuum and Czochralski grown crystals are different. As would be expected, both Ce^{3+} (347 nm) and F_1^+ (600 nm) centre luminescence bands are observed in the emission spectra of the vacuum grown crystals, see figure 4. In the study of crystals with a different ratio of light yields in the Ce^{3+} 5d–4f emission band and the F_1^+ emission band, we observed that the presence of F_1^+ centres does not have a quenching effect on the Ce^{3+} emission light yield. This is shown in figure 5 which presents the 5d–4f luminescence light yield as a function of the ratio η_R/η_B; η_B represents the light yield in the blue Ce emission band and η_R that in the red F_1^+ emission band. The Ce^{3+} light yield is, within error, independent on the ratio η_R/η_B. The small variations in η_B are probably related to technological factors such as small variations in the Ce concentration or the optical properties of the crystals.

In the Czochralski grown crystals, one observes Ce^{3+} luminescence only; the V_c^- centres do not luminesce at room temperature, and the concentration of F_2^+ centres, which are
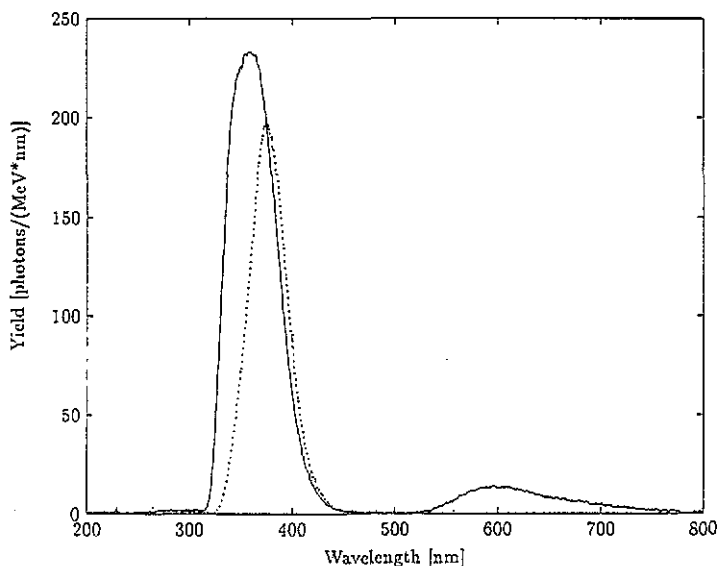
Figure 4. X-ray excited luminescence spectra of YAP:Ce single crystals: full curve, crystal grown by the method of horizontally oriented crystallization, 0.2 mass% Ce^{3+}, dimensions $10 \times 10 \times 1$ mm^3; dotted curve, Czochralski grown crystal, 0.5 mass% Ce^{3+}, dimensions $\varnothing 22 \times 2.6$ mm^3. The crystals were continuously excited by x-rays at room temperature, and the light yield is expressed as the number of photons created per megaelectronvolt of absorbed x-ray energy per nanometre wavelength interval.
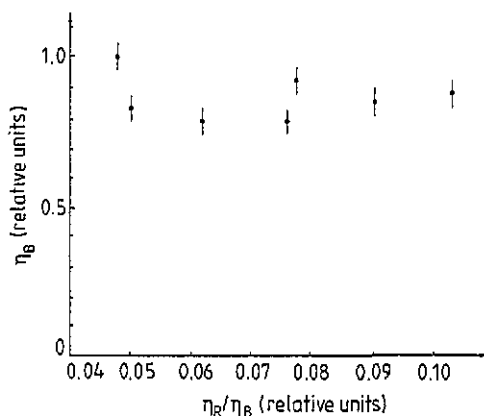

Figure 5. The integral Ce^{3+} luminescence light yield η_B at room temperature of YAP single crystals grown by the method of horizontally oriented crystallization in vacuum as a function of the ratio η_R/η_B.

located near cation vacancies, is small. The F$_2^+$ emission band can be observed under photoexcitation. Due to the presence of V$_c^-$ centres with their absorption band at $\nu_7 = 30\,000$ cm^{-1}, the light yield of the Czochralski grown YAP:Ce crystals is always lower than that of the vacuum grown crystals at the same Ce concentration. This can be observed in figure 4, in which the short-wavelength part of the Ce^{3+} emission band of

the Czochralski grown crystal is evidently absorbed by the V_c^{-1} centres. The absolute integral light yield of the Ce luminescence of the vacuum grown crystal is about 14 000 photons per megaelectronvolt of absorbed x-ray energy, which is about 37% of that of NaI(Tl$^+$) scintillation crystals. The Czochralski grown crystal shows 9200 photons MeV^{-1}.

Investigation of a great number of YAP:Ce samples grown by different methods revealed a correlation between the integral light yield of the Ce^{3+} luminescence band and the absorption intensity in the region $\nu > 27\,000$ cm^{-1}. Since the band at $\nu_7 = 30\,000$ cm^{-1} and the additional absorption band in the region $\nu > 35\,000$ cm^{-1}, see figure 2(b), provide an indirect indication of the Ce^{4+} concentration, we introduce the ratio

$$\alpha = \frac{K_1(33\,700 \text{ cm}^{-1})}{K_2(37\,730 \text{ cm}^{-1})}.$$

K_1 is proportional to the Ce^{3+} concentration whereas K_2, pertaining to the absorption strength at the minimum between the two main Ce^{3+} absorption bands, is a measure of the Ce^{4+} concentration. The parameter α basically represents a measure of the distribution of cations in YAP crystals doped with Ce. In a sense it is similar to the FOM parameter [16] used to characterize the quality of crystals employed for producing frequency tunable lasers. The integral Ce^{3+} luminescence light yield η_B as a function of the parameter α is shown in figure 6. One observes that substitutional Ce^{4+} defects in Ce^{3+} doped YAP crystals have a significant effect on the light yield. Crystals grown by the Czochralski method in an inert gas atmosphere are usually characterized by α values smaller than four. They require additional heat treatment in order to obtain an optimal Ce^{3+} luminescence intensity.
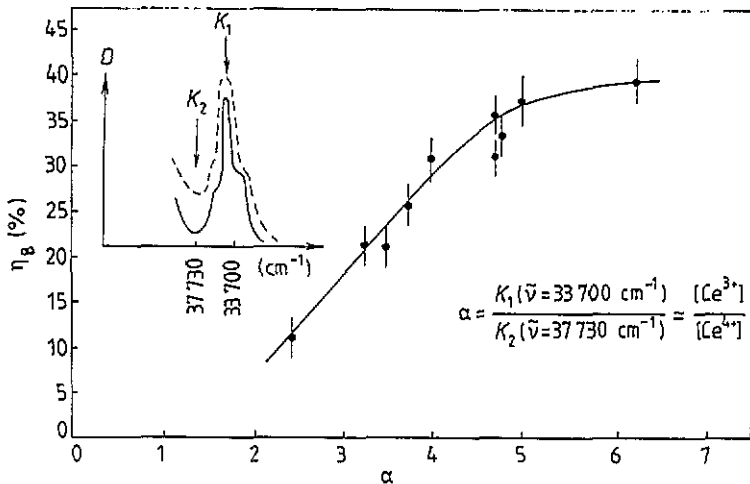

Figure 6. Integral Ce^{3+} light yield η_B of YAP:Ce single crystals as a function of the optical absorption ratio $\alpha = K_1(33\,700 \text{ cm}^{-1})/K_2(37\,730 \text{ cm}^{-1})$ at room temperature. The light yield is expressed as a percentage of the light yield of an NaI(Tl) scintillation crystal. The inset shows the location of K_1 and K_2 in the absorption (D) spectrum.

Figure 7 shows the scintillation decay spectra of YAP:Ce crystals excited by means of 662 keV γ-rays. The first 100 ns of the decay spectrum of the vacuum grown crystal is described well by an exponentially decaying function with characteristic decay time of $\tau =$
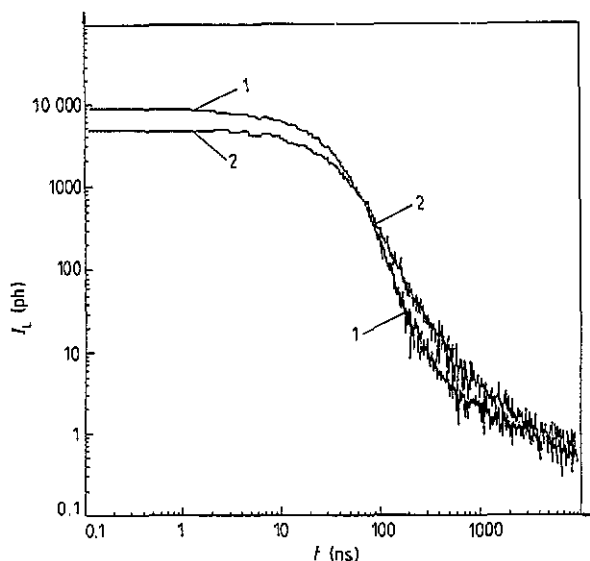
Figure 7. Scintillation decay time spectra of YAP:Ce single crystals grown by the method of horizontally oriented crystallization (1) and the Czochralski method (2) at room temperature. The crystals were excited by means of 662 keV γ-quanta.

32 ns. A slow-decay component dominates in the microsecond region. A value of about 30 ns is typical for the radiative lifetime of the excited 5d state of Ce^{3+} ions in ionic crystals [7]. Apparently, the excitation of the Ce^{3+} ions takes place in the sub-nanosecond time scale after excitation by a γ-quantum. The Czochralski grown crystal shows a somewhat slower decaying luminescence which is less well described by a single exponential function. This is probably due to delayed excitation of Ce^{3+} centres.

Summarizing, we conclude that substitutional defects related to the incorporation of Ce^{4+} ions in the YAP:Ce crystals cause a more pronounced decrease of the scintillation efficiency than the colour centres formed in these crystals during growth in vacuum. The vacuum grown crystals therefore show better scintillation properties than do the Czochralski grown crystals.

Acknowledgments

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