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A Single Crystal of $YAlO_3$: Ce^{3+} as a Fast Scintillator in SEM

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Summary

A new single-crystal scintillator intended for applications in a scanning electron microscope (SEM) is presented. It is a single-crystal disc of yttrium aluminium perovskite activated by trivalent cerium free of traces of Fe ions. The single crystals of $YAlO_3$: Ce^{3+} (YAP: Ce^{3+}) were prepared by the Czochralski method in a reducing atmosphere of Ar and H_2 with an excess amount of Y^{3+} ions. Effective methods of purification and purity control of the raw material are described. The highest achievable concentration of Ce^{3+} ions in as grown crystals amounted to 0.3 wt%, concentration in the melt was 8–9 times higher. The best properties were found with samples of the maximum possible concentration of Ce^{3+}. Compared with the previous aluminate $Y_3Al_5O_{12}$: Ce^{3+} (YAG: Ce^{3+}) these samples showed higher efficiency, a shorter decay time of luminescence (40 ns) and an emission band in a more advantageous spectral region (378 nm). Because of high resistance to radiation damage, high chemical resistance and applicability to ultra-high vacuum it is also suitable for detection of other kinds of ionizing radiation.

Introduction

Scintillators activated by Ce^{3+} possess a short decay time. For this property they have found acceptance in SEM for the detection of secondary and backscattered electrons. A number of basic lattices of oxides and sulphides were studied to be used for Ce^{3+} activation. However, the best results were obtained with yttrium silicates and aluminates. Yttrium silicate (P 47 phosphor) is used as powder exclusively, whereas aluminates can be applied both as powders and as single crystals. The merits of yttrium aluminate single crystals used as scintillators in SEM are their high resistance to electron beam radiation damage, good efficiency and signal-to-noise ratio and their suitability for ultra-high vacuum applications.

We have focussed our attention on single crystals of a pseudobinary system of Y_2O_3-Al_2O_3 in which three compounds are known to be convenient for Ce^{3+} activation. These are garnet – $Y_3Al_5O_{12}$ (YAG), perovskite – $YAlO_3$ (YAP) and monoclinic $Y_4Al_2O_7$ (YAM). The utilization of the single crystal of YAG: Ce^{3+} for detection of electrons in SEM was discussed in a previous paper (*Autrata* et al. 1978). The interest

paid to the cerium activated single crystal of perovskite structure is motivated by the properties reported for its polycrystalline form:

1. Shorter decay time of luminescence compared with garnet (τ_{YAG} = 70 ns, τ_{YAP} = 30 ns),
2. higher radiation efficiency (η_{YAG} = 4%, η_{YAP} = 7%) and
3. shorter wavelength of the light emission maximum ($\lambda_{max\ YAG}$ = 550 nm, $\lambda_{max\ YAP}$ = 370 nm) (*Takeda* et al. 1980).

If a single crystal of YAP: Ce^{3+} is used as a scintillator in SEM, its most important parameters are its spectral characteristics, efficiency, decay time, lifetime and applicability to ultra-high vacuum. Measurements were made in an adapted electron microscope in which the beam of primary electrons, not secondaries as in SEM, was used for excitation of luminescence in the scintillator. Electrons were incident on the scintillator surface with 10 keV energy and current density of 4 × 10^{-8} Acm^{-2}. The electron beam diameter was 3 mm for efficiency measurement and 0.5 mm for other measurements. For measurements of emission spectra an appropriately modulated light signal was detected after passage through the SPM 1 mirror monochromator (VEB Carl Zeiss Jena) with the help of a 9558B photomultiplier (EMI) and a 232 B lock-in nanovoltmeter (Unipan). Cathodoluminescence decay was measured in the pulse mode of operation using a repeated frequency of 1 kHz and an excitation pulse of 10 μs duration. The detection was effected by means of a fast photomultiplier 65 PK 415 (Tesla) and a sampling oscilloscope S 7–12 (SU). The decay time of the measuring system was less than 5 ns.

Scintillator preparation

Yttrium aluminium perovskite and yttrium aluminium garnet in single-crystal form share several properties that make them useful as highly efficient active laser and scintillator materials (*Thornton* et al. 1969, *Weber* et al. 1969). *Abell* et al. (1974) proved that YAP was metastable and during preparation turned into YAG and an unidentified phase. *Takeda* et al. (1980) solved these problems and prepared YAP: Ce free of undesirable phases.

Luminescence efficiency as well as other pertinent parameters of an oxide crystal are substantially lowered by the presence of impurities and the colour centres. In comparison with YAG, YAP can be coloured relatively easily. Nominally, undoped YAP turned yellow after annealing in oxygen or after UV or γ irradiation (*Antonov* et al. 1973) and those doped

with neodymium and iron group ions change their colour from violet to red (*Antonov* et al. 1974, *Arsenev* et al. 1974). The anomalous colouration differs from crystal to crystal and also seems to be dependent on the Y$_2$O$_3$: Al$_2$O$_3$ ratio of the initial material. Similarly, there are great differences in the parameters of YAP: Ce^{3+} scintillators. The aim of this paper is to describe the correlation between colour centre formation in undoped YAP and cathodoluminescence of YAP: Ce^{3+} single crystals and to characterize the luminescence properties of YAP: Ce^{3+} free of traces of iron ions.

YAP: Ce^{3+} single crystals were prepared by the Czochralski method using Mo crucibles and 98% Ar + 2% H$_2$ protective atmosphere. Raw material of 5 N purity was used. All the crystals were prepared using a melt containing 0.2–0.3% surplus of Y$_2$O$_3$ which enabled us to suppress the formation of YAG microcrystals on the surface of the YAP crystals. Undesirable iron content below 10^{-4} wt % coming from the initial material or a new crucible may be indicated in these crystals free of Ce^{3+} ions as a red colouration appearing after annealing in oxygen (Fig. 1).
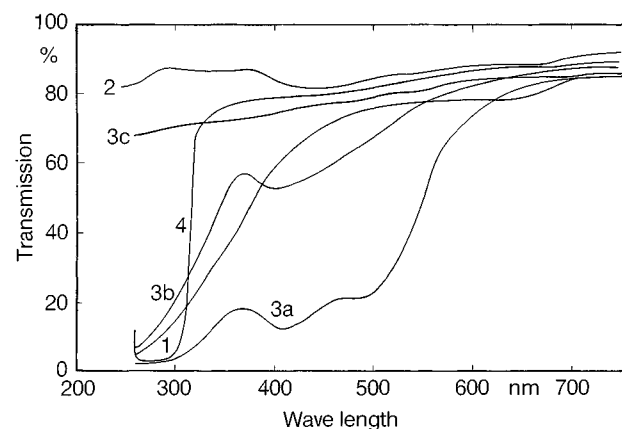

Fig. 1   Transmission spectra of YAP crystal plate of 1.5 mm thickness containing superfluous Y^{3+} ions. 1 = as grown; 2 = hydrogen annealed (1600°C, 3 h); 3 = oxygen annealed (1600°C, 3 h): a) crystal grown using a new raw material with iron concentration 6 × 10^{-4} wt %; b) raw material melted 20 h at 1950°C, iron concentration 2 × 10^{-4} wt %; c) raw material melted 60 h at 1950°C, iron undetected; 4 = as sample 3a but doped with ≈ 10^{-5} wt % Ce^{3+}.

Crystals grown from the stoichiometric melt showed relatively weak absorption and the same luminescence properties if doped with Ce^{3+}. Similar colouration as in the case of the crystals rich in Y^{3+} ions may be evoked in exactly stoichiometric YAP by Nd^{3+} + Fe^{3+} ions (*Kvapil Jo.* et al. 1980), but Nd^{3+} ions prolong the decay time of YAP: Ce^{3+} as in the case of YAG: Ce^{3+}. On the contrary, Ce^{3+} ions effectively eliminate this

type of absorption connected with Fe content, but the light output of a YAP: Ce^{3+} scintillator annealed in any atmosphere strongly decreases with increasing Fe concentration (Fig. 2).

Prolonged (40–50 h) melting of the raw material under the protective atmosphere decreases the Fe concentration from $\simeq 10^{-3}$ wt % to values undetectable by emission spectroscopy and neutron activation analysis, i.e. $< 1.5 \times 10^{-4}$ wt %, and good YAP: Ce^{3+} scintillator crystals may be grown from such a melt. Ce dopage also stabilizes the YAP phase to a greater extent than the superfluous Y$_2$O$_3$. These described phenomena may be explained as follows:

An excess of Y^{3+} in the crystal lattice causes the concentration of Al vacancies to be increased. Al vacancies and their oxygen neighbourhoods serve as electron donors. A released electron is trapped by Fe^{3+} which is partially converted to Fe^{2+}. It is well known that the presence of a transient element in a two valence state causes the intensive colouration of the matrix. The traces of Ce^{4+} in the oxygen annealed YAP: Ce prevent the formation of the Fe^{2+} and cause the colouration of Fe containing samples to be supressed. The structure of YAP containing no AlO$_4$ groups (ligands) as e.g. YAG, in the neighbourhood of Ce ions allows a strong Ce-Fe interaction resulting in effective luminescence quenching if compared, for example, with YAG.

The preparation of scintillation single crystals of YAP: Ce^{3+}, therefore, necessitates, accomplishing technological operations such as will eliminate the presence of Fe ions. For use in a detector it is necessary to cut the as grown single crystal of YAP containing $> 10^{-3}$ wt % Ce^{3+} of 30 mm diameter and 100 mm high into discs which are carefully polished at one base and mat-ground at the other to prevent Fresnel reflections from occurring when the light leaves the scintillator (*Schauer* and *Autrata* 1979). The discs of 0.4–1.0 mm thickness are then thermally treated in an oxidizing or reducing atmosphere. Before applying the single-crystal discs with the mat base to the light pipe the polished base is coated with a thin Al film (50 nm).

Absorption and emission spectra

A comparison of absorption spectra of YAP: Ce^{3+} and YAG: Ce^{3+} in 350–750 nm region is given in Fig. 2. The absorption spectrum of YAP: Ce^{3+} is characteristic of a very strong absorption band lying at energies just below the absorption edge (260–330 nm). The emission spectrum of YAP: Ce^{3+} corrected for sensitivity of the photomultiplier used shows its characteristic emission band at the boundary between the ultraviolet and visible region of the spectrum; with a maximum lying at 378 nm, the height of which depends on the Fe content of the sample (Fig. 2). The FWHM (50 nm) is much less than in the case of YAG: Ce^{3+} (145 nm). In the spectral region above 450 nm undesirable maxima occur which are caused by traces of Nd.

For the application considered here the single-crystal scintillator must be not only an efficient source of signal photons, but also an efficient light pipe in the spectral region of its own emission. It follows from the characteristic of the emission and absorption spectra in Fig. 2 that the YAP: Ce^{3+} scintillator shows a self-
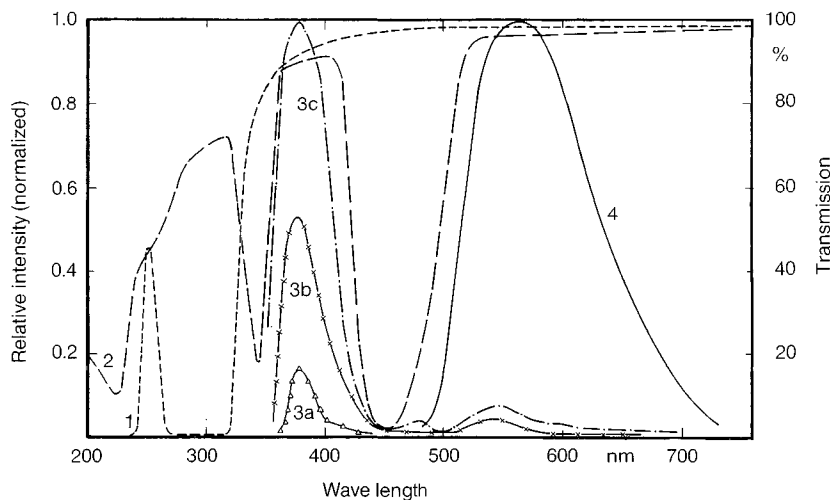

Fig. 2 Transmission spectra of 1 = YAP: Ce^{3+} of 0.37 mm thickness and 2 = YAG: Ce^{3+} of 0.41 mm thickness. Emission spectra of 3 = YAP: Ce^{3+}: a) crystal grown using a new raw material with iron concentration 6×10^{-4} wt %; b) raw material melted 20 h at 1950°C, iron concentration 2×10^{-4} wt %; c) raw material melted 60 h, iron undetected; 4 = YAG: Ce^{3+}.

absorption which is not negligible. On the basis of our measurements, it was calculated by numerical integration that single-crystal discs of perovskite of 10 mm diameter and 0.5 mm thickness provide a 20% self-absorption under the assumption of directionally homogenous photon emission whereas, for example, garnet discs of the same dimensions show only a 9% absorption. This fact must be taken into account when scintillator thickness is to be chosen.

From the point of view of the spectral sensitivity of photomultipliers usually used in SEM, the emission spectrum of YAP: Ce^{3+} is more advantageous than that of YAG: Ce^{3+} (*Kvapil* et al. 1980). A photomultiplier with increased sensitivity in the long-wave region (for example an S 20 photocathode recommended for YAG: Ce^{3+}) is not required.

Efficiency

Scintillator efficiency is generally expressed as radiant efficiency, which is defined as the ratio of the emitted light energy to the energy of the incident electron beam. The measurement of absolute radiant efficiency is very fastidious, and for practical use a relative quantity related to a generally known phosphor is quite sufficient.

Results of relative efficiency measurements of iron-free single-crystal aluminates of YAP: Ce^{3+} uncorrected for self-absorption are given in Table 1. The commercially available phosphor P 47 (Sylvania Chemical No. 23347-20) with a light emission maximum at 430 nm and 6% radiant efficiency (*Gomes de Mesquita* and *Bril* 1969) was used as a standard. In order to make conditions of light output from the scintillator comparable with the P 47 standard, parts of the single crystals of YAP: Ce^{3+} and YAG: Ce^{3+} were crushed to powders consisting of grains of uniform size. In such a way differences between detection efficiencies for the single-crystal and the powdered samples could be determined. The powdered samples were prepared by the sedimentation technique, the powder surface density being 2 mg/cm². They were covered with an organic film and then coated with a thin aluminium film.

The efficiency of the powdered samples decreases during the measurement, probably due to a certain radiation damage. This can be seen in Table 1 when comparing the initial value of efficiency with that obtained after three hour operation. The resistance to radiation damage shown by single-crystal samples is much better. The radiation damage depends on the current intensity in the exciting electron beam. Using a low current density (10 nA/cm^{-2}) the powdered samples of YAP: Ce^{3+} show little change in efficiency after 3 hours. Using a current density of 1 $\mu A/cm^2$, the effi-

Table 1 Relative cathodoluminescent efficiency of powder and single-crystal aluminates.

Relative efficiencies are given in per cent of the initial corrected value of P 47 standard (Sylvania No. 23447-20). Excited electron beam density was 4 × 10⁻⁸ Acm^{-2}.

Sample		Relative efficiency %			
		Measured		Corrected for PMT	
		Initial	After 3 h	Initial	After 3 h
Powder	P 47 standard	84.1	72.8	100	86.3
	YAG: Ce^{3+}	129	120	215	199
	YAP: Ce^{3+}	170	161	204	195
Single crystal	YAG: Ce^{3+} treated in H_2	142	138	237	229
	YAP: Ce^{3+} treated in H_2	188	183	226	217
	YAP: Ce^{3+} treated in O_2	120	116	144	140
	YAP: Ce^{3+} as grown	161	156	194	189

ciency decreased to 60% of its initial value after five hours operation.

Much better results are achieved with single-crystal discs of YAP: Ce^{3+} whose efficiency changes by only a few percent within the time interval of 3–5000 hours even if current densities of 10 $\mu A/cm^2$ are used.

In addition to the measured values of the relative efficiency, values corrected for spectral sensitivity of PMT used are also given in Table 1. The corrected values were calculated from the measured efficiency, emission spectra and spectral sensitivity of the PMT (65 PK 415 Tesla). The difference between the measured and corrected values of the relative radiation efficiency confirms a more advantageous optical matching of the single crystal of YAP: Ce^{3+} to the photomultiplier used.

The dependence of intensity of the cathodoluminescent emission of YAP: Ce^{3+} as well as YAG: Ce^{3+} scintillators on the density of the excitation current of electrons and on their energy increases nearly linearly. The intensity of the cathodoluminescent emission is also affected by the concentration of the cerium activator. An increased Ce^{3+} concentration in the YAP: Ce^{3+} lattice (measured in the concentration region of 1.3 × 10⁻³ – 3 × 10⁻¹ wt % of Ce^{3+}) brings about an

increase in the intensity of the characteristic emission band (378 nm).

Ce^{3+} ions are incorporated into the lattice of an YAP single crystal more easily than into YAG. The dependence of cathodoluminescent efficiency on Ce^{3+} ions concentration in YAG shows a saturation at concentrations higher than 2×10^{-2} wt % according to our measurements. In the case of YAP, such a state of saturation in the Ce^{3+} concentration region of up to 2×10^{-2} wt % does not occur (*Autrata* et al. 1982). It is evident from Table 1 that cathodoluminescent efficiency is favourably increased by additional thermal annealing of YAP: Ce^{3+} discs in H_2 atmosphere. The increase amounts to 15% with regard to an unannealed, as-grown single crystal of YAP: Ce^{3+}. On the contrary, annealing in an O_2 atmosphere brings about a decrease in cathodoluminescent efficiency. Only YAG: Ce^{3+} scintillators are subjected to thermal annealing in O_2 atmosphere because, besides the undesirable decrease of cathodoluminescent efficiency, a shorter decay time is achieved in this way. The decay time of YAP: Ce^{3+} scintillators does not change by annealing in an O_2 atmosphere.

The intensity of the characteristic emission band is also slightly dependent on temperature. In the temperature range 300–500 K, the change of the initial intensity amounts to 10%.

It should be noted that the comparison of scintillation efficiencies of samples given in Table 1 serves for basic orientation in judging material properties. It does not provide a true picture of the performance of the detector system. *Comins* et al. (1978) introduced a very useful criterion called "detective quantum efficiency" (DQE). It is based on measurements of variations of the signal/noise properties of the detector system and characterizes much better the system performance because it comprises initial scintillator light output, degradation rate, detector design, operating conditions, etc. On the basis of the characteristics reported by *Comins* and *Thirlwall* (1981) for the powder P 47 phosphor and a plastic scintillator and on the basis of our preliminary measurements, the DQE of single-crystal YAP scintillator is assumed to reach a high value. This work is the subject matter of our interest.

Kinetic properties

A very important property of the scintillator in the scintillation-photomultiplier detector is the decay time of luminescence. Its value decides if television frequencies may be used for object scanning. The measurement of the decay time is important not only

for practical applications, but it also constitutes a means for determining the mechanism of the luminescent process. Under the term decay time, we understand the time interval after stopping excitation during which the emission intensity decreases to a $1/e$ value (e being the base of the natural logarithm).

The decay characteristics of the monocrystalline YAP: Ce^{3+} are given in Fig. 3. For the sake of comparison, decay characteristics of a very fast powder phosphor P 47 are also figured. The plotted decay characteristics involve all emission bands of a spectrum. This better illustrates the scintillator properties with regard to the specific SEM application. For the purpose of physical interpretations, however, it is necessary to measure the decay times of individual emission bands separately, even for the non-characteristic bands.

The decay time of the sample of the single crystal of YAP: Ce^{3+} shown in Fig. 3 amounts to 40 ns and the afterglow measured 5 μs after stopping excitation is 1%. The decay time of the powder sample P 47 is 38 ns. Unlike the P 47 phosphor, the decay characteristic of YAP: Ce^{3+} is a non-exponential curve.

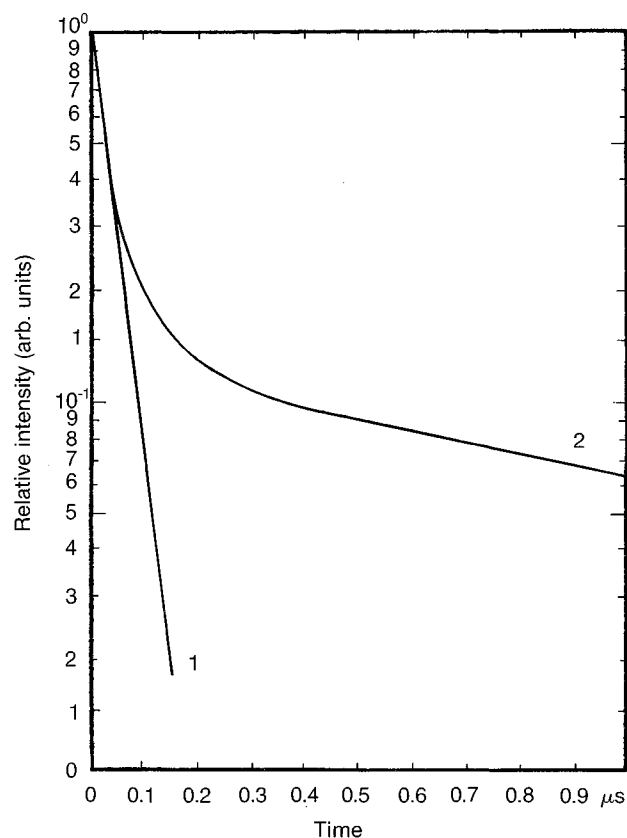Fig. 3   The luminescence decay characteristics. Excitation pulse duration was 10μs. 1 = phosphor P 47; 2 = single crystal YAP: Ce^{3+}.

The time characteristics of YAP: Ce^{3+} can be affected by an alteration in the content of trivalent cerium in the single crystal lattice. Samples with high concentrations of Ce^{3+} (0.3 wt %) whose decay times do not exceed 40 ns are the fastest. On the other hand, samples having a low concentration of Ce^{3+} (1.3×10^{-3} wt %) have decay times of at least one order higher.

The decay time of the single crystal YAP: Ce^{3+} is not affected by additional annealing in an oxidizing or reducing atmosphere as in the case of single crystals of YAG: Ce^{3+} (*Kvapil* et al. 1981, *Robbins* et al. 1979). Samples annealed for periods of 5 hours at 1500°C in oxidizing or reducing atmospheres showed decay characteristics identical with initial parameters.

Conclusion

Yttrium aluminium perovskite activated by trivalent cerium and free of Fe ions belongs to a new generation of monocrystalline scintillators. Single crystals of YAP: Ce^{3+} must be free of the traces of Fe ions that effectively quench the luminescence of Ce^{3+}. Melting the raw material under a reducing atmosphere causes this undesirable impurity to be removed. The advantages of the new scintillator are that it has a very short decay time, a high relative radiant efficiency, a suitable wavelength of characteristic emission, high resistance to radiation damage, chemical resistance and is compatible with ultra-high vacuum. It is suitable for SEM applications, but can also be used for the detection of other kinds of ionizing radiation.

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