CATHODOLUMINESCENT PROPERTIES OF SINGLE CRYSTALS FOR S(T)EM DETECTORS

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INTRODUCTION

The cathodoluminiscent (CL) emission spectrum, CL efficiency (emission intensity), and decay time are three basic scintillator parameters of a scintillation detector for a scanning electron microscope and/or a scanning transmission electron microscope - S(T)EM. They are important not only for the estimation of suitability of the single crystals application in S(T)EM but also for the physical analysis of CL. Besides the scintillator efficiency, the scintillator decay time is the decisive characteristic for a high detective quantum efficiency (DQE), and the emission spectrum is an important characteristic for the spectral matching to the photomultiplier tube (PMT).

INVESTIGATED CRYSTALS AND EXPERIMENTAL ARRANGEMENT

At our laboratory, some tens of different single crystal CL materials were measured. Of these, single crystals of cerium activated yttrium aluminum garnet (YAG:Ce - $Y_3Al_5O_{12}:Ce^{3+}$), cerium activated yttrium aluminum perovskite (YAP:Ce - $YAlO_3:Ce^{3+}$), cerium activated yttrium silicate ($Y_2SiO_5:Ce^{3+}$, which chemically corresponds to the powder phosphor P47), and europium activated calcium fluoride ($CaF_2:Eu^{2+}$) were chosen as the most interesting ones for S(T)EM applications. Cathodoluminescent (CL) properties of the scintillators investigated were measured using a computer assisted CL apparatus [1]. For spectral measurement, the CL signal was spectrally decomposed by a mirror monochromator, picked up by a PMT at the output slit of this monochromator, and measured using a lock-in nanovoltmeter. The individual instruments were connected to the general purpose interface bus (GPIB, IEEE-488), and the measuring apparatus was controlled by a personal computer. The measuring and processing software which contained correction algorithms was written in programming languages Turbo Pascal and Basic.

SURVEY OF SINGLE CRYSTALS PROPERTIES

Emission spectra

The CL emission spectra of YAG:Ce, YAP:Ce, P47 and CaF_2:Eu single crystals are shown in Fig. 1, and the spectral sensitivities of S 11 and S 20 photocathodes used are presented in Fig. 2. The emission spectra are corrected for the spectral sensitivity of the PMT used and each is normalized with regard to its maximum value. This gives better information about the position of the emission bands but at the same time makes the comparison of intensities impossible. For each single crystal, the position of the maximum of the emission band and the value of the full width of the half maximum (FWHM) together with the value of the spectral matching to the S 20 photocathode used, as well as to S 11, are given in Table I. It follows from the results summarized in the table that the CaF_2:Eu and YAP:Ce single crystals show the best and the worse spectral matching, respectively, to the S 20 PMT used. However, the spectral matching of YAP:Ce could be markedly increased by using the PMT with the quartz entrance window. It is not the photocathode itself but the glass entrance window that causes the low spectral sensitivity of PMT in the short wave spectrum region.

The YAG:Ce is the only single crystal that is suitable for CL screens for direct observation. Unlike other investigated single crystals, it emits light in the yellow spectrum region, and this is very favourable for the human eye. On the contrary, this is unfavourable for conventional PMTs

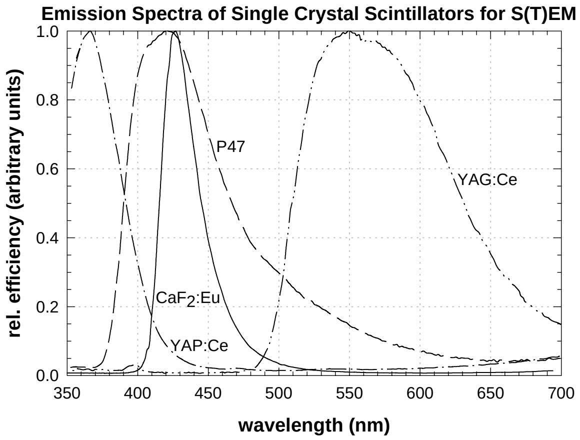

Figure 1 Normalized cathodoluminescent spectra of single crystal scintillators for S(T)EM.

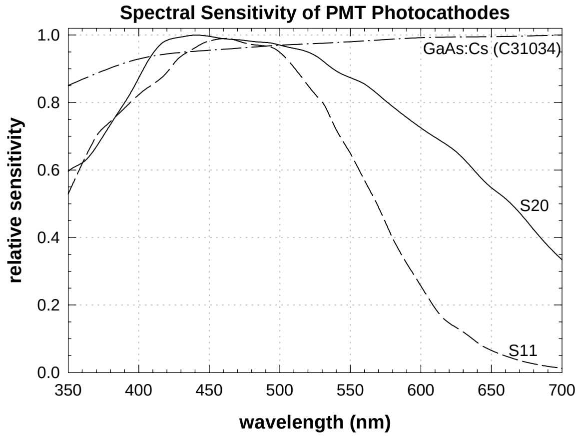

Figure 2 Normalized spectral response of the sensitivity of the photocathodes used.

Table I Spectral properties of single crystals for S(T)EM

single crystal	spectral characteristic maximum* (nm)	FWHM** (nm)	S20 PMT matching*** (%)	S11 PMT matching**** (%)
YAG:Ce	560	122	73	45
YAP:Ce	366	52	60	58
P47	420	77	85	80
CaF2:Eu	426	30	92	88

*position of the maximum of the main emission band.

**full width of the half maximum of the main emission band

***matching to the spectral response of S20 photocathode

****matching to the spectral response of S11 photocathode

with alkali photocathodes. In the case of YAG:Ce, it is necessary to use the S 20 photocathode (its long wave spectrum region differs from that of S 11). All other single crystals investigated can also work with the S 11 photocathode. In addition to the characteristic broad yellow emission band with a maximum at 560 nm, the YAG:Ce shows a very weak emission in the blue, violet and UV spectrum regions. This weak emission which is more marked for specimens with a low activator concentration has a sharp maximum at 400 nm which is superimposed on the broad emission band with a maximum in the UV region, i.e. beyond the capabilities of the measuring device used.

Efficiency

For all applications in S(T)EM, high CL efficiency is required. The relative CL efficiency of the investigated single crystals is shown in Table II. The values of this quantity are always related to the corrected value of the YAG:Ce single crystal. The as measured integral (spectrally non-decomposed) efficiency includes the influence of the PMT photocathode spectral sensitivity. This quantity is interesting from the viewpoint of application in scintillation detectors where the

Table II Efficiency of single crystals for S(T)EM

single crystal	relative efficiency* corrected** for PMT	as measured*** (S20 PMT)	estimated**** (S11 PMT)	forming***** after 3 hours (%)
YAG:Ce	100	73	45	2.8
YAP:Ce	142	85	82	1.2
P47	126	107	101	0.8
CaF2:Eu	131	120	115	2.4

*related to the corrected value of YAG:Ce
**corrected for the spectral response of the S20 photocathode used
***uncorrected for the spectral response of the S20 photocathode used; measured 30 min. after the start of
****estimated if the S11 photocathode were used
*****efficiency decreasing during given time (related to the initial value).

effects of the PMT photocathode cannot be avoided. In contrast to this, the efficiency corrected for the spectral sensitivity of the S 20 photocathode used is interesting from the physical point of view, and it allows estimation of changes expected in connection with an application of some other photocathode, as shown in column 4 of Table II.

For all single crystal CL materials, the degradation of efficiency was very low. For electrons with an energy of 10 keV and a current density of 4×10^{-8} Acm^{-2}, the forming of the efficiency of all single crystals measured was observed. During the first three hours, the decrease in efficiency was less than 3% as evident from the last column of Table II. The efficiency decrease was only temporal to a great extent. So, when the measurement was repeated later, similar results, but within a shorter time period, were obtained, and no additional degradation took place.

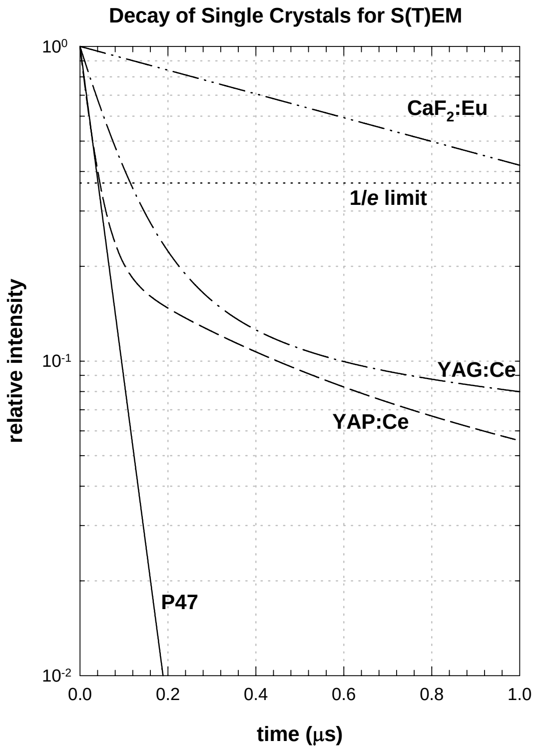

Figure 3 Decay characteristics of single crystals for the S(T)EM. Excitation pulse duration 10 :s.

Decay time

Typical CL decay characteristics for YAG:Ce, YAP:Ce, P47 and CaF_2:Eu single crystals are shown in Fig. 3. The values of the decay time and afterglow are given in Table III. The typical excitation pulse duration was 10 :s. Both yttrium aluminate single crystals (YAG:Ce and YAP:Ce) have multiexponential decay characteristics. On the other hand, P47 and CaF_2:Eu single crystals have single exponential decay curves, with measured decay times of 41 ns and 1.2 :s, respectively. The measured decay time of YAG:Ce is 110 ns and the afterglow (measured 5 :s after the end of excitation) amounts to 2 %. For YAP:Ce, the measured decay time is only 45 ns

Table III Decay properties of single crystals for S(T)EM

single crystal	decay time* (ns)	time characteristic corrected decay time** (ns)	afterglow*** (%)
YAG:Ce	110	103	2
YAP:Ce	45	38	0.5
P47	41	34	unmeasurable
CaF2:Eu	1200	1200	1.3

*uncorrected for the time response of the measuring equipment

**corrected for the time response of the measuring equipment

***intensity measured 5 :s after the end of excitation

and the afterglow amounts to less than 1 %. In fact, with respect to the fall time of the pulse of the excitation electron beam (5 ns) and the fall time of PMT (2 ns), the short-term decay component must be corrected by subtracting approximately 7 ns of the fall time of the measuring equipment. The short-term component of the CL decay of both yttrium aluminate single crystals depends only negligibly on the duration of excitation. On the contrary, the long-term component of the CL decay depends strongly on the duration of excitation, so that for a very short excitation the afterglow of YAG:Ce and YAP:Ce can be one order and at least two orders lower, respectively. This is advantageous for applications in S(T)EM electron detectors operating at the TV rate, because the images with a rich topographic content can be of higher quality.

CONCLUSION

Unfortunately, all single crystals that have their CL decay time shorter than 100 ns (which is the condition when the TV scan frequency is used) contain oxygen and just this group of single crystals belongs to those with the least efficiency [2, 3]. This means that calcium fluoride, which is the most efficient of the four chosen, has only limited applicability because its decay time constant is 1.2 :s. The greatest advantage of YAP:Ce single crystals and P47 is that they are the fastest (38 ns and 34 ns, respectively). Especially, they have no such a marked component of long persistent luminescence as the YAG:Ce single crystals have. The only disadvantage of YAG:Ce single crystals is their speed which can be behind the limit for the TV rate in some cases. It is therefore necessary to search for a way to shorten the decay time of YAG:Ce scintillators.

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