The study of inorganic scintillating materials

G N Dudkin, S I Kuznetsov, V N Padalko and M S Syrtanov
Tomsk Polytechnic University, Tomsk 634050, Russia

E-mail: smit@tpu.ru

Abstract. The procedure for measuring the temporal characteristics and light output of inorganic scintillating materials excited by β-, γ-, and α-particles from radioactive sources is described. Results of measurements of characteristics are presented for ~30 scintillating compounds including cerium-doped yttrium silicate and scandium borate; europium-doped strontium phosphate; cerium-doped strontium silicate, calcium silicate and magnesium calcium silicate, etc. Upon β- and γ-excitation, cerium-doped scandium borate gives the highest light output with a fluorescent lifetime of 40 ± 4 ns. The highest light output for α-excitation was from cerium-doped yttrium aluminum perovskite, with a fluorescent lifetime of 29 ± 3 ns.

1. Introduction

Inorganic scintillating materials are widely used in detectors for diverse applications ranging from high energy physics to nuclear medicine [1-2]. Better understanding of various scintillation mechanisms has led to innovative new materials for both gamma-ray and neutron detection, and the concept of scintillator design and engineering has emerged, whereby materials are optimized according to the scintillation properties needed by specific applications [3]. Although certain incremental improvements may still be achieved in each property, the main challenge then becomes to find a scintillator material that has a correct combination of properties to meet the needs of a given application rather than to find a scintillator with a single outstanding characteristic.

Intensive efforts to find and study new substances with higher light outputs, shorter fluorescent lifetimes, higher transparencies, smaller radiation lengths, etc., still continue [4-11]. The fluorescence decay lifetime of a scintillating substance is usually determined by the statistical method of single-photon counting [12]. The results obtained by this technique are independent of the shape and dimensions of samples under investigation. Measurements of the light output from substances are carried out under conditions that allow comparisons with results from other samples. For this purpose, crystals are grown to have similar dimensions (~1 cm³). Identical conditions of light collection on a photomultiplier tube are provided, and the relative light yield is determined by the peak height of the total absorption of γ-quanta of known energy [13,14]. However, it is much easier and less expensive to synthesize a new substance in a powdered form. Based on the results of preliminary tests, one may decide whether or not to grow crystals. Thus, in [14], relative scintillation efficiency and fluorescence decay time were studied using a pulsed (τ<1 ns) monochromatic (Eγ = 22 keV) X-ray beam from the Brookhaven National Laboratory synchrotron source. A powdered scintillating compound was placed in a quartz cuvette and its light output was measured by comparing its response to radiation to the response of a bismuth germanate (BGO) crystal allowing for light absorption in the powder and the
efficiency of interaction of X-rays with the material. As a result, approximately a hundred new inorganic compounds were investigated within a short period.

Using radioactive sources that are more readily available makes it possible to perform measurements with various types of ionizing radiation. In this work, we measured the characteristics of powdered inorganic scintillators using β-, γ-, and α-sources.

2. Measurement procedure

The samples used in the study were prepared by the deposition of a fractionated luminophore powder from aqueous silicate suspension on a 22 mm diameter glass substrate. The 8–10 μm thick luminophore layer made of a powder with a grain size of 2–3 μm provides, on the one hand, identical conditions of light transmission for different samples and elimination of light loss in the scintillator and, on the other hand, necessary efficiency of detection of γ-photons with energy of ~20 keV.

In the device operating in the statistical mode of single-photon counting (figure 1), sample 1 and radioactive source 3 (90Sr, 238Pu) are placed between two photomultiplier tubes.

One of them, PMT1, is in optical contact with the sample and detects light pulses whose leading edges give the start mark for intervals measured. The stop signal is provided by the other photomultiplier, PMT2. PMT-130 photomultipliers with a sensitivity range of 200–650 nm, and good single-electron counting characteristics were used for the measurements. Attenuation of light burst intensity required for single-photon counting on PMT2 is accomplished with diaphragm 5 and by varying distance L from the sample. Since radioactive source 3 prevented the direct passage of light from the sample to PMT2, mirror 2 and reflector 4 were applied to provide light collection.

![Figure 1. Diagram of the setup for measurements of fluorescence lifetime of scintillating materials. PA is the preamplifier; CFD1 and CFD2 are the riding-threshold shapers, TS1 and TS2 are the threshold shapers; CC1 and CC2 are the coincidence circuits; TAC is the time-to-amplitude converter; ADC is the analog-to-digital converter; DAPС is the data acquisition and processing complex; Δt1, Δt2, and Δt3 are the matching delay lines; (1) sample, (2) mirror, (3) radiation source; (4) reflector, (5) diaphragm.](image)

To form the start signal, a two-threshold detection system is used that includes a constant-fraction discriminator, threshold shaper (TS1), and coincidence gate. The constant-fraction discriminator with a low (~2 photoelectrons) threshold accomplishes accurate timing of the instant of excitation of the sample. In the case of β-activation, the timing starts from the pulse front of the Cerenkov radiation produced in the glass substrate and determining the front of the overall light pulse. The threshold of shaper TS1 is established at a level of ~0.5 of the signal peak height.

Pulses from PMT2 (stop channel) after the amplification with a preamplifier pass to discriminator CFD2 having the detection threshold in the “valley” of single electron pulse distribution. Relative efficiency of detection of scintillation flashes by this channel is established at a level of 1/20 by the
ratio of counts from the coincidence circuits $CC_1$ and $CC_2$, thus providing the probability of <2.5% for detecting many-electron events.

The start and stop signals are transmitted to the time-to-amplitude converter (TAC) triggered by a strobe pulse from the coincidence circuit $CC_2$. Timing of signals is accomplished with cable delay lines. Threshold shapers $TS_2$ and $TS_3$ are used to restore the front and the amplitude of the start and stop signals, which are distorted by delay lines. Measurements on the luminophore-free glass substrate used as a Cerenkov light emitter gave the time resolution of the device as $\sigma = 0.68$ ns.

Fluorescent lifetime’s $\tau_2$ and $\tau_3$ are determined as parameters of approximation of time spectrum by two exponentials (figure 2)

The total uncertainty of determination of $\tau_2$ does not exceed 10%. In order to verify the procedure, we measured the fluorescence lifetime of the KS-425-l commercial luminophore, which is a constituent of a type V-2 electrooptical transducer, upon excitation with monoenergetic electrons. To synchronize the instant of luminophore excitation with the start pulse, a silicon carbide light-emitting diode was used (flash duration <2 ns) which illuminates the photocathode of the electrooptical transducer.

The value measured in this manner agrees, within the limits of accuracy, with the $\tau_2$ and $\tau_3$ values obtained upon excitation with a $^{90}$Sr $\beta$-source.

To measure the afterglow intensity $F$ of a substance, an additional delay ($\Delta\tau_3$) of 5 μs was introduced to the start channel. Time spectra with and without the delay are built-up during the same period, and the $F$ value is determined as the ratio of the number of events in these spectra within the interval $\tau_2$ for the given substance. The accuracy of determination of $F$ is ~20%.

The light yield from samples is measured by two methods. The first one is based on the use of a $^{90}$Sr $\beta$-source. For $\beta$-particles, the ionization energy loss $dE/dx$ in a thin layer of a scintillator depends mainly on its density. Relative light yield accurate to within ~20% is determined from the ratio of counts in the start and stop channels (introducing a correction for density of the material).

![Figure 2. Temporal spectra of fluorescence decay of scintillating materials upon $^{90}$Sr $\beta$-excitation: (1) KS-425-l (two-exponential decay law), (2) and YAlO$_3$:Ce (one-exponential decay law).](image-url)
More accurate determination of the light yield is performed with the use of γ-sources of low energies: \(^{65}\text{Zn}\) \((E_\gamma = 8.1\ \text{keV})\), \(^{113}\text{Sn}\) \((E_\gamma = 24.7\ \text{keV})\), and \(^{241}\text{Am}\) \((E_\gamma = 13.2\ \text{keV}; E_\gamma = 17.8\ \text{keV}; E_\gamma = 59.5\ \text{keV})\) [15]. The relative light yield for α-particles was determined by using a \(^{238}\text{Pu}\) source. Because the range of α-particles from this source exceeds the thickness of scintillation screens under study, the mode of total energy absorption is achieved by varying the distance from the α-source to the luminophore so that to obtain the required energy of α-particles at the expense of ionization loss in air.

3. Results

The characteristics of ~30 types of scintillating substances were measured on the apparatus. Tables 1 and 2 list these characteristics for β- or γ-excitation and for α-excitation, respectively. Rows 2–22 in Table 1 and rows 2–8 in Table 2 present the data on luminophores prepared in the Mendeleev University of Chemical Technology (the wavelengths at the maxima of emission spectra were also measured there). The YAlO₃: Ce crystal and Scandium borate, produced at the Research Institute of Nuclear Problems of Belarusian State University (Minsk), was kindly presented by the Joint Institute for Nuclear Research (Dubna).

**Table 1.** Scintillating materials and their characteristics on β-excitation

| \(\#\) | Scintillator type | \(\lambda_{\text{max}}, \text{nm}\) (color) | \(\tau_2, \text{ns}\) | \(\tau_1, \text{ns}\) | \(L_{\text{rel}},\%\) | \(F,\%\) |
|-------|------------------|-----------------|-----------------|-----------------|----------------|----------------|
| 1     | KS-425-1 \([\text{Y}_3\text{SiO}_5 : \text{Ce (1.5 wt\%)}]\) | 410             | 38±4            | 51±4            | 100            | ~0.03         |
| 2     | \(\text{Y}_2\text{SiO}_3: \text{Ce + BaF}_2\) | 410             | 39±4            | 86              | 0.03           |
| 3     | \(\text{Y}_2\text{SiO}_3: \text{Ce (2 wt \%)}\) | 380             | 35±3            | 29              | 0.03           |
| 4     | \(2\text{YPO}_4 : \text{Ce}\) | 365             | 33±3            | 5               | 0.6            |
| 5     | \(\text{Y}_{0.8}\text{La}_{0.2}\text{PO}_4: \text{Ce}\) | 365             | 39±4            | 6               | 0.03           |
| 6     | \(\text{SrO-SiO}_2 : \text{Ce (0.04 mol \%)}\) | 410             | 48±5            | 27              | 0.31           |
| 7     | \(\text{SrO-SiO}_2 : \text{Ce (0.04 mol \%)}\) with additional calcination at, \(t = 1250°C\) for 1 h | 410             | 45±4            | 5               | 1              |
| 8     | \(\text{Sr}_2\text{(PO}_4\text{)} :\text{Eu}_2\text{O}_3 (0.6 wt\%) t = 100°C} \) | 425             | 375±35          | 89              | —              |
| 9     | \(\text{Sr}_2\text{(PO}_4\text{)} :\text{Eu}_2\text{O}_3 (0.6 wt\%) t = 1200°C} \) | 425             | 395±40          | 89              | —              |
| 10    | \(\text{Sr}_2\text{(PO}_4\text{)} :\text{Eu}_2\text{O}_3 (0.6 wt\%) t = 1300°C} \) | 425             | 405±40          | 83              | —              |
| 11    | \(\text{Sr}_2\text{(PO}_4\text{)} :\text{Eu}_2\text{O}_3 (1.2 wt\%) t = 1300°C} \) | 425             | 389±40          | 44              | —              |
| 12    | \(3\text{Ca}_{2}\text{SiO}_5: \text{Ce (0.1 mol \%)}\) with additional calcination at, \(t = 1250°C\) for 1 h | 410             | 39±4            | 22              | 0.3            |
| 13    | \(3\text{Ca}_{2}\text{SiO}_5: \text{Ce (0.1 mol \%)}\) with additional calcination at, \(t = 1250°C\) for 1 h | 410             | 47±5            | 4               | 0.6            |
| 14    | \(2\text{CaO-MgO-2SiO}_2: \text{Ce, calcination for 1.5 h, } t = 1250°C\) | 380             | 48±5            | 4               | 2              |
| 15    | \(2\text{CaO-MgO-2SiO}_2: \text{Ce, calcination for 3 h, } t = 1250°C\) | 380             | 47±5            | 4               | 0.7            |
| 16    | \(2\text{CaAl}_{2}\text{O}_3-\text{SiO}_2: \text{Ce (0.015 mol \%)}\) | 400             | 56±5            | 4               | —              |
| 17    | \(\text{CaZrO}_3: \text{Ti}\) | White | 276±30          | 37              | —              |
| 18    | \(\text{BaZrO}_3: \text{Ti}\) | White | 40±4            | 31              | —              |
| 19    | \(\text{ScBO}_4: \text{Ce (0.8 mol \%)}\) | 390             | 33±3            | 62              | 0.03           |
| 20    | \(\text{ScBO}_4: \text{Ce (2.5 mol \%)}\) | 390             | 32±3            | 60              | 0.02           |
| 21    | \(\text{ScBO}_4: \text{Ce (1.5 mol \%)} + \text{BaF}_2 (0.3 mol \%)\) | 390             | 38±3            | 67*             | 0.03           |
| 22    | \(\text{ScBO}_4: \text{Ce (1.5 mol \%)} + \text{BaF}_2 (1 mol \%)\) | 390             | 39±4            | 75*             | 0.04           |
| 23    | \(\text{ScBO}_4: \text{Ce (Minsk)}\) | 393             | 40±4            | 156*            | 0.03           |
| 24    | \(\text{YAlO}_3 : \text{Ce (3 x 3 x 0.1 mm}^3\text{ crystal) (Minsk)}\) | 347             | 32±3            | 98*             | 0.03           |
| 25    | \(\text{CsI(Tl) (3 x 3 x 0.6 mm}^3\text{ crystal) (Minsk)}\) | 430             | 710±50          | 100*            | —              |
Table 2. Scintillating materials and their characteristics on α-excitation

| №  | Scintillator type | λ_{em}, nm (color) | τ₂, ns | τ₃, ns | L_{α3},% | F, % |
|----|------------------|-------------------|-------|-------|---------|------|
| 1  | KS-425-1         | 410               | 29±3  |       | 100     | 0.03 |
| 2  | Y₂SiO₅: Ce, t = 1350°C | 410              | 28±4  |       | 69      | 0.03 |
| 3  | Y₂SiO₅: Ce, t = 1350°C | 410              | 30±3  |       | 116     | 0.03 |
| 4  | Y₂SiO₅: Ce + NF₄, t = 1350°C | 410             | 20±2  |       | 69      | 0.02 |
| 5  | Y₂SiO₅: Ce + BaF₂, t = 1350°C | 410             | 26±2  |       | 89      | 0.02 |
| 6  | Y₂SiO₅: Ce + BaF₂, t = 1300°C | 450             | 24±2  |       | 57      | 0.03 |
| 7  | Y₂SiO₅: Ce + BaF₂, t = 1300°C, White |                   | 21±2  |       | 121     | 0.02 |
| 8  | ZrGeO₄: TiP       | 430               | 110±10|       | 75      | 2     |
| 9  | KO-425 (Y₂SiO₅: Ce, Gd) | 410            | 45±4  |       | 72      | 0.04 |
| 10 | ScBO₃: Ce (Minsk) | 393               | 37±4  |       | 131     | 0.03 |
| 11 | YAlO₃: Ce (Minsk) | 347 [8]           | 29±3  |       | 216     | 2     |

4. Conclusion

An analysis of the results shows that the highest light yield upon β-excitation is provided by cerium-doped scandium borate (a sample from Minsk). Its light yield is higher than that of CsI(Tl). For α-excitation, the cerium-doped yttrium aluminum perovskite (YAP:Ce) crystal has unique light yield characteristics. For scintillators intended for the identification of charged particles, the α/β ratio is of practical importance. We determined this ratio for Y₂SiO₅: Ce, YAlO₃: Ce, and ScBO₃: Ce as 0.19, 0.46, and 0.16, respectively. Tables 1 and 2 also show the dependence of luminescent lifetimes of inorganic scintillators on the type of particles exciting the scintillations. This time is shorter for α than for β-excitation; the difference is especially pronounced in the case of the KS-425-1 luminophor.

Acknowledgements

The research has been supported by the project VIU_NU_174_2014 in the context of the Competitiveness Improvement Program of the Tomsk Polytechnic University.

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