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SCINTILLATION PROPERTIES OF LEAD SULFATE*

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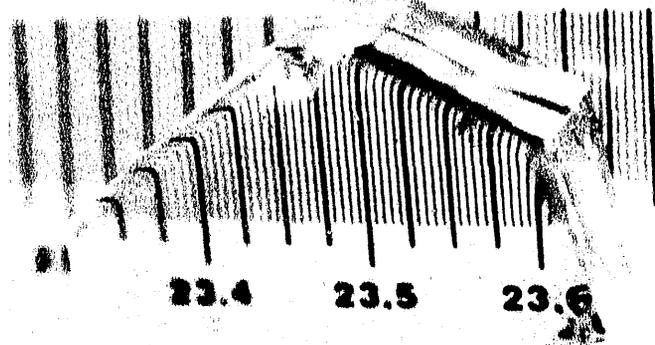
Abstract

We report on the scintillation properties of lead sulfate (PbSO_4), a scintillator that shows promise as a high energy photon detector. Its physical properties are well suited for gamma detection, as it has a density of 6.4 gm/cm^3 , a $1/e$ attenuation length for 511 keV photons of 1.2 cm, is not affected by air or moisture, and is cut and polished easily. In 99.998% pure PbSO_4 crystals at room temperature excited by 511 keV annihilation photons, the fluorescence decay lifetime contains significant fast components having 1.8 ns (5%) and 19 ns (36%) decay times, but with longer components having 95 ns (36%) and 425 ns (23%) decay times. The peak emission wavelength is 335 nm, which is transmitted by borosilicate glass windowed photomultiplier tubes. The total scintillation light output increases with decreasing temperature from 3,200 photons/MeV at $+45^\circ \text{C}$ to 4,900 photons/MeV at room temperature ($+25^\circ \text{C}$) and 68,500 photons/MeV at -145°C . In an imperfect, 3 mm cube of a naturally occurring mineral form of PbSO_4 (anglesite) at room temperature, a 511 keV photopeak is seen with a total light output of 60% that of BGO. There are significant sample to sample variations of the light output among anglesite samples, so the light output of lead sulfate may improve when large synthetic crystals become available.

1. INTRODUCTION

There has been increasing interest in developing a new scintillator for high energy photon detection. Such a scintillator would combine the stopping power of BGO, the luminosity of NaI(Tl) , and the speed of BaF_2 . Lead sulfate (PbSO_4) has been reported to possess a fast decay time, a stopping power similar to that of BGO, and a low light output [1], but these measurements were mostly qualitative and were made either in synthetic powders or naturally occurring crystals of PbSO_4 . This paper provides quantitative measurements of the emission spectrum, scintillation decay time, and temperature dependence of the light output in synthetic crystals, as well as the absolute light output of PbSO_4 in a naturally occurring crystal. The emission spectrum and scintillation decay time measurements are performed as a function temperature between $+50^\circ \text{C}$ and -150°C .

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Figure 1: Crystal of anglesite, a mineral form of PbSO_4 . The units of the scale are inches.

The material properties of PbSO_4 are attractive for use as a gamma radiation detector. Its density is 6.4 g/cm^3 , resulting in, for 511 keV photons, an attenuation length of 1.2 cm and a photoelectric effect cross section fraction of 42%. It is not hygroscopic, is colorless, transmitting light down to 250 nm, and is slightly birefringent with indices of refraction of 1.88, 1.82 and 1.89 [2]. While large synthetic crystals are not yet available, natural crystals such as in Figure 1 can be both large and transparent.

1.1 Previous Measurements of PbSO_4

Scintillation in anglesite, a naturally occurring mineral form of lead sulfate, was first reported by Firk in 1990 [1]. Based on observation of oscilloscope traces, two decay time components were reported: a fast ($<10 \text{ ns}$) component that contained between one-fourth and one-third of the total light output and a longer (150 ns) component that contained the remainder of the light. The total light output was reported to be three times that of cerussite (a naturally occurring mineral form of lead carbonate). Using the value of 9% of BGO for the light output of cerussite [3], this implies a light output of 27% of BGO (or 2200 photons/MeV) for anglesite.

An independent experiment [4] measured the scintillation decay lifetime from the surface of 99.999% pure PbSO_4 powder excited by 20 keV x-rays, and found components having 7.4 ns (7% of the total light output), 34 ns (21%), and 168 ns (46%) decay times, with the remainder of the light in a $>10 \mu\text{s}$ component. The emission spectrum was measured to peak at 350 nm, and the total light output crudely measured to be 52% of BGO.

Finally, lead sulfate powder was reported by Blasse [5,6] to luminesce when excited with ultraviolet light. The emission spectrum peaks at 360 nm, and the total light output at room temperature is greater than 50% of its intensity at liquid helium temperatures (4.2° K).

1.2 PbSO₄ Samples Measured

Large, clear crystalline samples of synthetic PbSO₄ are not currently available. Therefore, most of the measurements presented herein were made with small (0.5 – 1 mm typical dimension) synthetic crystals made with the method described by Blount [7]. These crystals were analyzed with x-ray fluorescence spectroscopy and found to contain less than 0.002% impurities. For ease of handling, a lead sulfate “target” was made by filling a 3 mm diameter, 3 cm long fused silica cuvette with these small crystals. This “target” has the stopping power and fluorescent properties of a larger synthetic crystal, but with reduced light collection efficiency and uniformity. A thermocouple was placed among these small crystals to monitor the temperature of the sample. For the measurement where uniformly high light collection is necessary (*i.e.* the total light output measurement), an anglesite crystal from Chihuahua, Mexico was used.

2. EMISSION SPECTRUM

The emission spectrum of synthetic PbSO₄ was obtained using a 0.125 meter Jarrell-Ash MonoSpec 18 monochromator with a 1200 line/mm grating blazed for 300 nm. The entrance and exit slits of this monochromator were 500 μm wide, resulting in a spectral resolution of 12 nm. The 511 keV photons from a 0.7 mCi ⁶⁸Ge source were used to excite the lead sulfate “target” described in Section 1.2. The “target” was placed at one focus of quartz optics that directed the emissions onto the entrance slit of the monochromator, and a quartz windowed Hamamatsu R-2059 photomultiplier tube (spectral range 200 to 600 nm) was placed at the exit slit in a thermally insulated enclosure cooled to -25° C to reduce dark current to less than 1% of the PbSO₄ signal at +25° C. The PbSO₄ “target” and a portion of the optics were in a separate, thermally insulated, temperature controlled enclosure. Two inches of lead shielding was placed between the radioactive source and the photomultiplier tube to prevent direct 511 keV photon interactions in the photomultiplier tube. The output of the photomultiplier tube was converted to a logic pulse with a Tennelec TC-454 constant fraction discriminator and counted with a Jorway 84 CAMAC scaler.

2.1 Emission Spectrum

The temperature of the “target” was set at +25° C and the resulting photomultiplier tube count rate is plotted, after background subtraction, as a function of

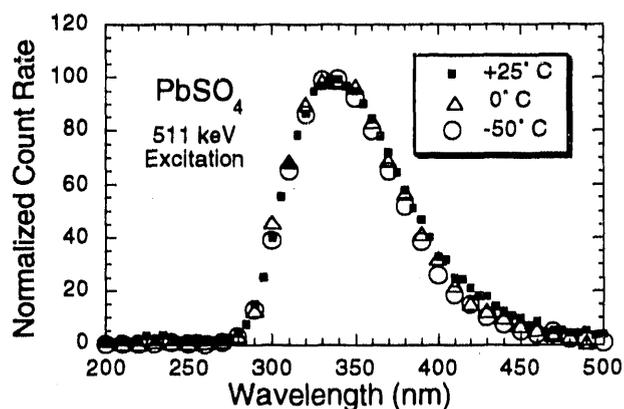


Figure 2: PbSO₄ emission spectra at several temperatures.

monochromator wavelength in Figure 2. This spectrum is not corrected for the spectral response of the photomultiplier tube or monochromator. The emission spectrum peak peaks at 335 nm, and drops to 10% of its maximum intensity at 290 nm and 450 nm. The paucity of light below the 300 nm cutoff of borosilicate glass implies that fused silica or UV glass windowed photomultiplier tubes are not necessary in order to collect the majority of the PbSO₄ scintillation light. This data agrees with the emission spectrum obtained with optical (<225 nm) excitation [6]. The emission spectrum measurement was repeated with the “target” at temperatures of 0° C and -50° C. As the data in Figure 2 shows, the shape of the emission spectrum is independent of temperature.

3. FLUORESCENT DECAY TIME

The fluorescent decay lifetime of synthetic PbSO₄ was measured using the delayed-coincidence method of Bollinger and Thomas [8], as modified by Moszynski and Bengtson [9]. A barium fluoride scintillator coupled to a Hamamatsu R-2059 photomultiplier tube provided a start signal, and another R-2059 photomultiplier tube placed 50 cm away from the sample provided the stop signal. As with the emission spectrum measurement, the PbSO₄ “target” was in a thermally insulated, temperature controlled housing and the single photon photomultiplier tube was cooled. A 0.7 mCi ⁶⁸Ge source provided the 511 keV photon pairs that excited both the BaF₂ scintillator and the PbSO₄ scintillator sample. Timing signals from both photomultiplier tubes were generated using a Tennelec TC-454 constant fraction discriminator, and the time difference between the start and stop signals was digitized a Tennelec 862 time to amplitude converter and a LeCroy 3512 analog to digital converter (ADC).

3.1 Decay Time Spectrum at Room Temperature

In order to span a large dynamic range, two decay timing distributions were accumulated. One covered a 360 ns range in 420 ps bins, while the other spanned a 8 μs range in 8.4 ns bins. This pair of data sets (shown in

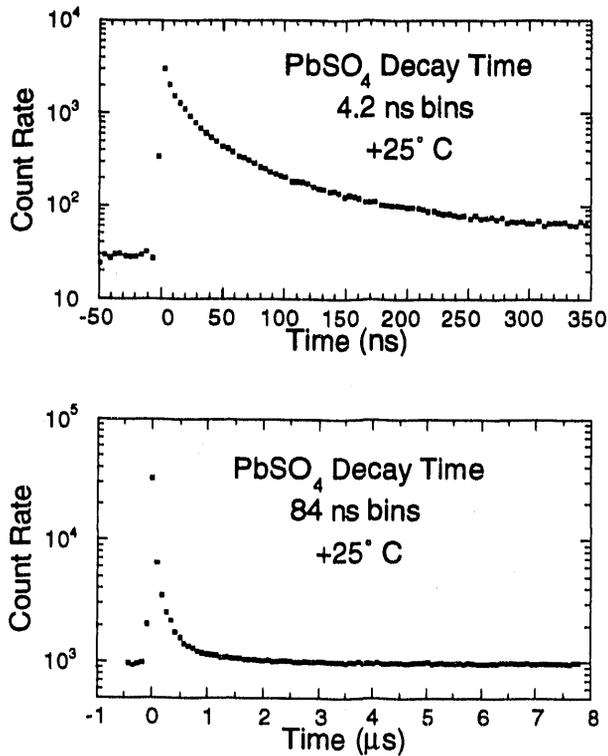


Figure 3: PbSO₄ decay time spectra at room temperature.

Figure 3 with the data binned more coarsely for clarity is simultaneously fit with a sum of four exponential decay lifetimes plus a constant background. The resulting fit implies that lead sulfate has significant fast components with 1.8 ± 0.3 ns (5%) and 19 ± 1.0 ns (36%) exponential decay times, but also has longer components having 95 ± 10 ns (36%) and 425 ± 31 ns (23%) decay times. There is no indication of the slow (>10 μ s) component measured in [4], even when the dynamic range was expanded to 200 μ s. The error bars on the lifetimes of the individual components are large because there are significant correlations in the fit, but the fit spectrum is indistinguishable from the data plotted Figure 3.

3.2 Decay Time Spectrum vs. Temperature

A pair of decay time data sets were collected at temperatures ranging from -130° C to $+40^\circ$ C, and each set simultaneously fit with the 4 component fit described above. The variation of the 4 decay lifetimes with temperature is plotted in Figure 4. While correlations again make it difficult to accurately measure individual lifetimes, the overall tendency is for the lifetimes to increase with decreasing temperature. The exception is tau 1 (the fastest component), which is roughly constant.

The relative intensities of each component also vary greatly as a function of temperature, and are plotted in Figure 5. Again, significant correlations between the components are present, but are smaller than the correlations between decay lifetimes. The overall trend is that

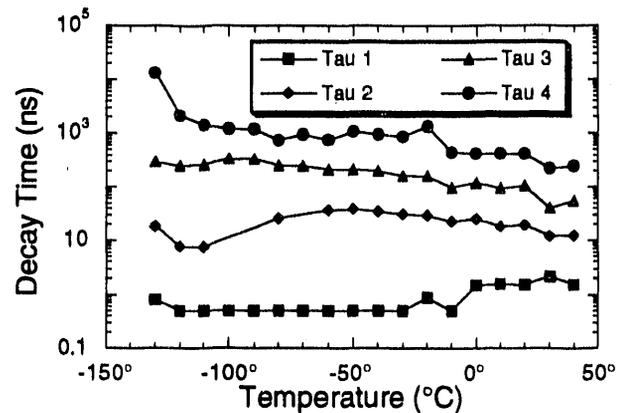


Figure 4: PbSO₄ decay component lifetimes vs. temperature.

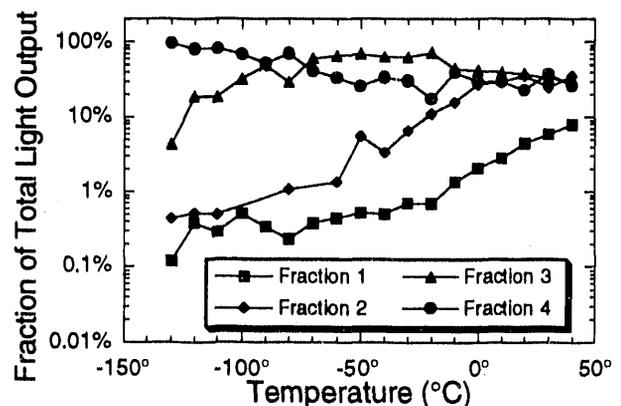


Figure 5: PbSO₄ decay component fractions vs. temperature.

the majority of the light is equally distributed among the three slowest components for temperatures above 0° C, and the two slower components dominate below 0° C.

4. TOTAL LIGHT OUTPUT

4.1 Light Output at Room Temperature

The total light output of natural crystal of anglesite from Chihuahua, Mexico was measured at $+25^\circ$ C by comparing its response to 511 keV photons to the response of a bismuth germanate (BGO) crystal under the same conditions. A 3 mm cube of anglesite was coated on five sides with a reflective coating of white Teflon tape, then optically coupled to a quartz-windowed Hamamatsu R-1306 photomultiplier tube with General Electric Viscasil 600M silicone fluid. The crystal was irradiated with 511 keV and 1.275 MeV photons from a ^{22}Na source, and the output of the photomultiplier tube amplified with a Tenclec TC-222 amplifier with 0.6 μ sec shaping time and digitized with a LeCroy 3512 ADC. The resulting pulse height spectrum

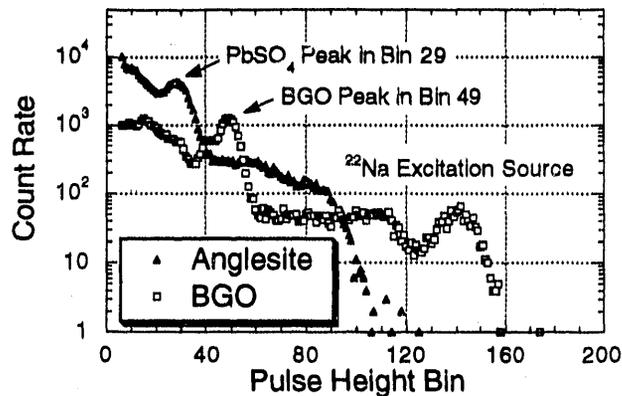


Figure 6: Photopeaks in anglesite and BGO.

is plotted (after pedestal subtraction) in Figure 6. The anglesite crystal was removed and the same experiment was performed on a 3 mm cube of BGO, and the resulting spectrum is also shown in Figure 6.

The photopeak corresponding to the 511 keV photon is seen in each plot in Figure 6. The 511 keV photopeak in anglesite is centered at a pulse height that is 60% of the 511 keV photopeak pulse height in BGO. Using the BGO light output of 8200 photons/MeV reported by Holl, *et al.* [10], this implies that the light output of anglesite is approximately 4900 photons/MeV. The full width at half maximum (FWHM) of the 511 keV photopeak in PbSO₄ is 40%, which is greater than a light output of 4900 photons/MeV implies, probably because of light collection non-uniformity due to imperfections in the crystal. This experiment was repeated with anglesite crystals from a number of additional locations (Tsumeb, South Africa; Mendip Hills, England; Phoenixville, PA; West Tasmania; and Morocco), and while wide variations in the total light output were observed, all had lower total light output than the Chihuahua crystal.

4.2 Light Output vs. Temperature

Since the decay time of PbSO₄ is temperature dependent, it is necessary to measure the total light output in a way that is insensitive to changes in the scintillation decay time. This was done by exciting the synthetic PbSO₄ "target" with a 0.7 mCi ⁶⁸Ge source and measuring the output current of the cooled photomultiplier tube with a Keithley 617 electrometer. The "target" was placed in the same thermally insulated, temperature controlled housing as was used in the emission spectrum measurement in Section 2, but the monochromator between the sample and the photomultiplier tube was removed and the quartz optics readjusted. Again, two inches of lead was placed between the source and the photomultiplier tube to minimize direct interactions in the photomultiplier tube.

The resulting photomultiplier tube current is shown, as a function of temperature, in Figure 7 after converting

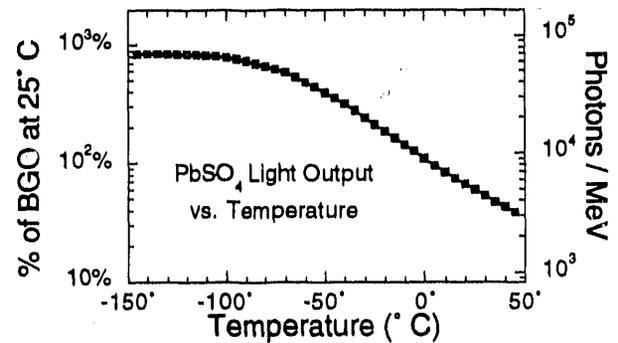


Figure 7: Lead sulfate light output vs. temperature.

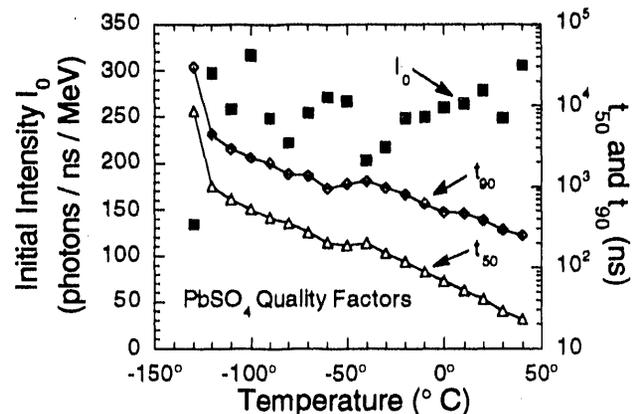


Figure 8: Lead sulfate initial intensity I_0 and times t_{50} , and t_{90} vs. temperature. See text for definitions.

to absolute light output using the previously measured light output of 4900 photons per MeV at 25° C. The light output increases exponentially with decreasing temperature until roughly -100° C, below which point the light output is essentially constant.

5. OPTIMAL OPERATING TEMPERATURE

It is difficult to determine the optimal operating temperature from the light output and decay lifetime values described above. Therefore we have computed, based on the fit parameters, several measures of the decay time distribution that describe the spectrum in terms that are useful when using scintillators as radiation detectors. First, we compute the initial intensity I_0 , which has units of number of photons per ns per MeV of incident energy. This number aids in estimating the attainable timing resolution of the scintillator. We also compute t_{50} and t_{90} , which are the times that it takes to emit 50% and 90% of the total number of photons. The t_{50} value helps estimate the amplifier shaping time, while t_{90} is useful in estimating the dead time of the scintillator. These values are plotted as a function of temperature for lead sulfate in Figure 8. For comparison, the values for I_0 , t_{50} , and t_{90} for BGO at 25° C are 39 photons per ns per MeV, 160 ns and 590 ns respectively.

Figure 8 shows that the initial intensity I_0 is approximately 250 photons/ns/MeV, independent of temperature, while t_{50} (t_{90}) increases from 23 ns (250 ns) to 8 μ s (30 μ s) with decreasing temperature. Thus, while the overall increase in the decay time with decreasing temperature increases the amplifier shaping time and dead time of a system using PbSO_4 , the increasing light output maintains a constant initial photon rate and so the timing resolution will not deteriorate with decreasing temperature.

6. SYNTHETIC CRYSTAL GROWTH

Although small (1 mm) crystals of synthetic lead sulfate have been grown and shown to exhibit good scintillation properties, most detector applications require significantly larger crystals. Growing large synthetic crystals is complicated because the decomposition temperature of PbSO_4 is lower than its melting point, and so conventional zone-refinement or Czochralski growth techniques cannot be used.

However, several crystal growth methods have produced synthetic lead sulfate crystals. The hydrothermal growth method, where PbSO_4 is dissolved in water at high temperature and pressure and crystallized in a lower temperature zone, may be capable of growing large crystals, but the growth rate may be quite slow. A flux growth method, where PbSO_4 is dissolved in another compound (the flux) and crystallized by lowering the temperature of the mixture, has produced centimeter sized crystals, but the optical quality of these crystals is poor because of numerous inclusions of the flux material. More development of these and other crystal growth processes is necessary before PbSO_4 scintillation crystals can be produced at a reasonable cost.

7. CONCLUSIONS

The scintillator PbSO_4 is an excellent detector for high energy gamma radiation, and could conceivably replace BGO for gamma detectors that require high stopping power, good timing resolution, and low dead time, such as those found in high energy physics experiments or PET cameras. It has approximately the same attenuation length and photoelectric fraction as BGO (1.2 cm and 42% for PbSO_4 , 1.1 cm and 43% for BGO), and the initial photon flux and the dead time are three times faster than BGO, while the light output at room temperature is 60% that of BGO. Both the decay time and the light output increase significantly as the temperature is reduced.

Further development is necessary before lead sulfate can be used as a practical radiation detector. Radiation damage studies must be made on PbSO_4 at a facility capable of simultaneously measuring the luminescence and absorption properties, but the greatest challenge is to produce large volume, optical quality crystals. While this promises to be difficult, encouraging progress has been

made in the last year, and the economics of this crystal growth process will probably decide whether PbSO_4 replaces BGO or remains a tantalizing possibility.

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