A Search for Scintillation in Doped Cubic Lead Fluoride Crystals

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***Abstract*—An effort was made to introduce scintillation light in lead fluoride crystals by selective doping. It was found that some rare earth ions doped in the lead fluoride crystal may serve as luminescence centers. The photo- and X- luminescence spectra, the decay time constants and the light outputs were measured for these doped samples. The decay time was found to be at a few milliseconds for these rare earth doped lead fluoride samples, which is too long to be useful for the homogeneous hadronic calorimeter detector concept with dual readout for future high energy physics experiments. Work to introduce scintillation in lead fluoride will continue.**

***Index Terms*—Crystals, luminescence, particle measurements, solid scintillation detectors.**

I. Introduction

INORGANIC crystal scintillators have played an important role in the construction of total absorption electromagnetic calorimeter (ECAL) for high energy physics experiments. Crystals have recently also been proposed to construct a homogeneous calorimeter, including both ECAL and hadronic calorimeter (HCAL) [1] for detectors at the international linear collider (ILC). This homogeneous hadronic calorimeter (HHCAL) detector concept removes the traditional boundary between ECAL and HCAL, so eliminates the dead materials in the middle of the hadronic shower development. It also takes advantage of the recently implemented dual readout approach to achieve good energy resolutions for hadronic jets by measuring both Cerenkov and scintillation light [2].

Because of the unprecedent volume (70 to 100 m^3) foreseen for such calorimeter [1], the crystal material must be dense (to reduce the volume), UV transparent (to effectively collecting the Cerenkov light) and allow a clear discrimination between the Cerenkov light and the scintillation light [3].

Cubic lead fluoride (β-PbF_2) crystal has a high density of 7.77 g/cm^3, a short radiation length ($X_0 = 0.93$ cm) and a short nuclear interaction length ($\lambda_I = 21$ cm). It has good UV transparency down to 250 nm. Its low melting point (824°C) and low material cost (1/3 of BGO) make it a potential cost-effective material for the HHCAL detector concept. Large size (20 cm long) PbF_2 crystals are available in the market. They were used as a Cerenkov material to construct an ECAL for the A4 experiment at the MAinzer MIcrotron (MAMI) facility at Mainz. Excellent energy resolutions were reported [4].

As a Cerenkov material cubic PbF_2 has been studied in details [5]. The only issue for the HHCAL application is that it is not a scintillator at room temperature. Luminescence was observed in PbF_2 single crystals at low temperature by several groups [6]–[8] for both orthorhombic (α-PbF_2) and cubic phases. Scintillation at room temperature was first reported by Derenzo *et al.* for orthorhombic powers [9], but with a very small intensity. Effort was made to introduce scintillation light into PbF_2 through phase transition (cubic to orthorhomic) during growth. Positive result was reported by Klassen *et al.* [10], but was not confirmed by Anderson *et al.* [11]. Observation of a fast photo- and x- luminescence in Gd doped PbF_2 crystals was first reported by Shen *et al.* [12], and was later confirmed by Woody *et al.* in a beam test at AGS [13].

In this work lead fluoride samples doped with various rare earth elements were grown by a modified Bridgman method.

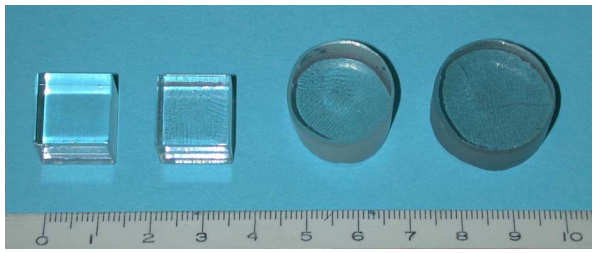

Fig. 1. A photo showing four lead fluoride crystal samples doped with various rare earth elements from SIC (left two cubes) and Scintibow (right two cylinders).

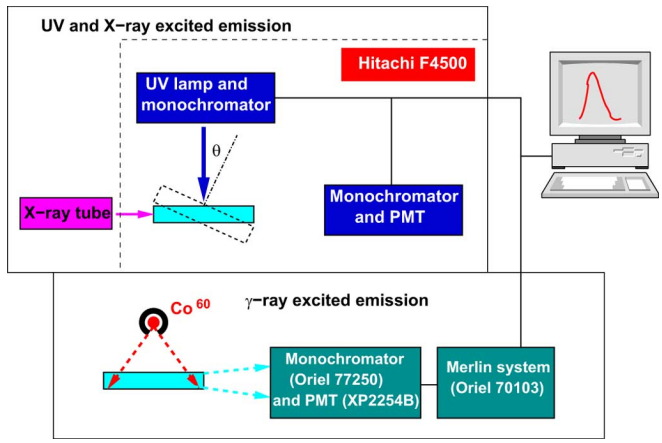

Fig. 2. The setup used for the photo- and x- luminescence measurement.

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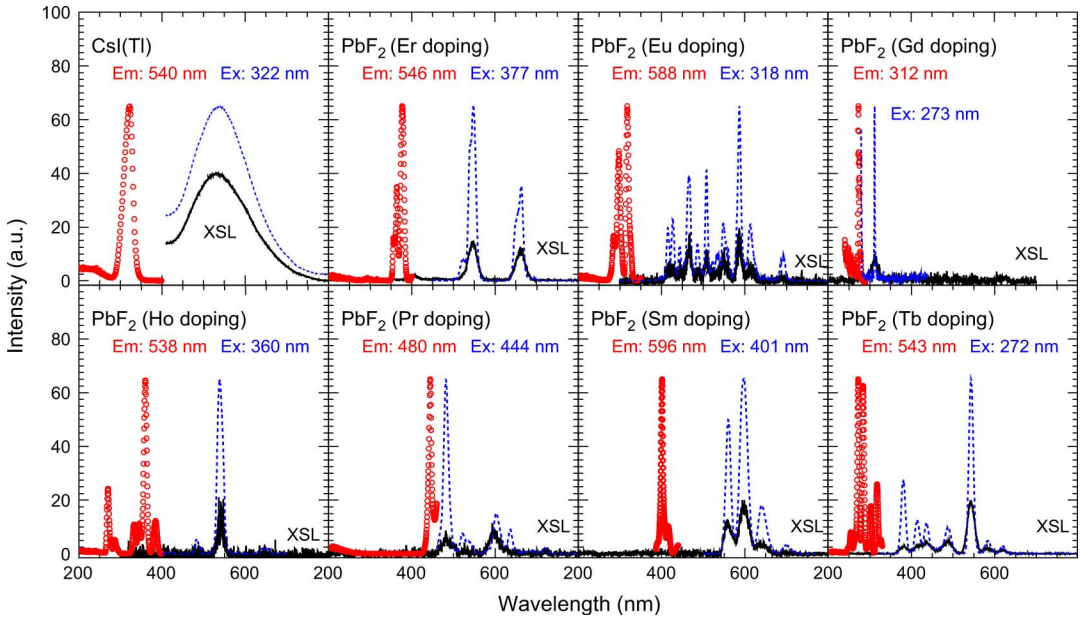

Fig. 3. The excitation (red dots) and Photo- (blue dashes) and X- (black lines) luminescence spectra are shown as a function of wavelength for the PbF_2 samples doped with Er, Eu, Gd, Ho, Pr, Sm and Tb as well as a reference CsI(Tl) sample.

The photo- and X- luminescence spectra, the decay kinetics and the γ-ray excited anode current and the pulse height spectra were measured for these samples.

A total of 116 PbF_2 samples doped with various rare earth elements were grown by a modified Bridgman method at Shanghai Institute of Ceramics (SIC) and Shanghai Scintibow Crystal Co., LTD. While classical platinum crucible was used at SIC for the crystal growth, graphite crucible was used at Scintibow. The SIC samples are cubes of 1.5 radiation length with six faces polished as shown in the left two samples in Fig. 1. Most Scintibow samples are cylinders with two end faces polished and have a dimension of ϕ 22$\times$15 mm as shown in the right two samples in Fig. 1. Because of the contaminations the crystal samples grown in the graphite crucible are less transparent than that in the platinum crucible. All samples are of cubic phase (β-PbF_2) as verified by the X-ray diffraction pattern (XRD).

II. Photo-and X- Luminescence Spectra

Photo- and X-ray luminescence spectra were measured by using a Hitachi F-4500 fluorescence spectrophotometer. Fig. 2 shows the setup used for this measurement. For the X-ray luminescence measurement an Amptek E3-T X-ray tube was run at 25 kV and 50 μA. Fig. 3 shows the excitation (red dots), the photo-luminescence (blue dashes) and the X-luminescence (black lines) spectra for the PbF_2 samples doped with Er, Eu, Gd, Ho, Pr, Sm and Tb as well as a reference CsI(Tl) sample. Although spectroscopic resolutions are different, the observed photo- and X- luminescence spectra are consistent for all samples. The spectra of PbF_2 samples doped with Eu, Pr and Sm were carefully checked, and no fast emission from $\mathrm{Eu2+}$, $\mathrm{Pr^{3+}}$ and $\mathrm{Sm^{2+}}$ were identified. The photo- and x- luminescence spectra observed in the Gd doped PbF_2 samples are consistent with previous publications by Shen [12] and Woody [13].

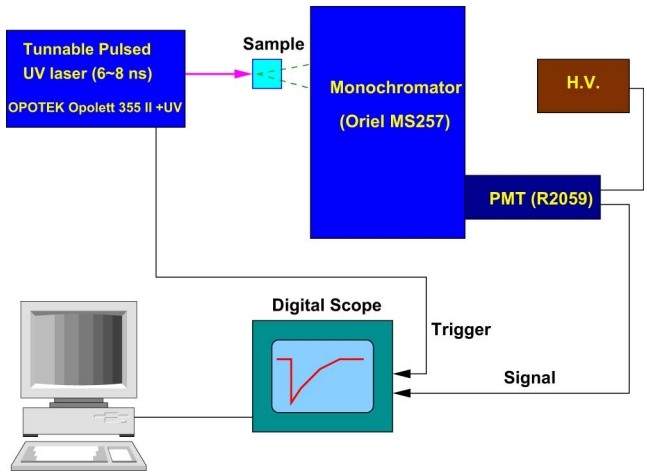

Fig. 4. The setup used for the photo-luminescence pulse shape and the decay time measurement.

III. Photo-Luminescence Decay Time Constant

The photo-luminescence decay time constant of these doped PbF_2 samples was measured by using a pulsed laser as the excitation source. Fig. 4 shows the setup used in this measurement. The UV light pulses of 6–8 ns width from an *Opotek Opolette 355 II + UV* tunable laser was used as the excitation source. The wavelength of the laser was set at the peak values of the excitation spectra shown in Fig. 3. The photo-luminescence light from these samples went first through an Oriel MS257 monochromator then to a Hamamatsu R2059 PMT. The wavelengths of the monochromator was set at the peak values of the emission spectra shown in Fig. 3. The decay time constants were determined by an exponential fit to the pulse shape. Fig. 5 shows the photo-luminescence pulse shape (blue circles), the corresponding exponential fit (red lines) and the decay time constant for the PbF_2 samples doped with Er, Ho, Eu, Sm and Tb as well as a reference CsI(Tl) sample. The photoluminescence intensity

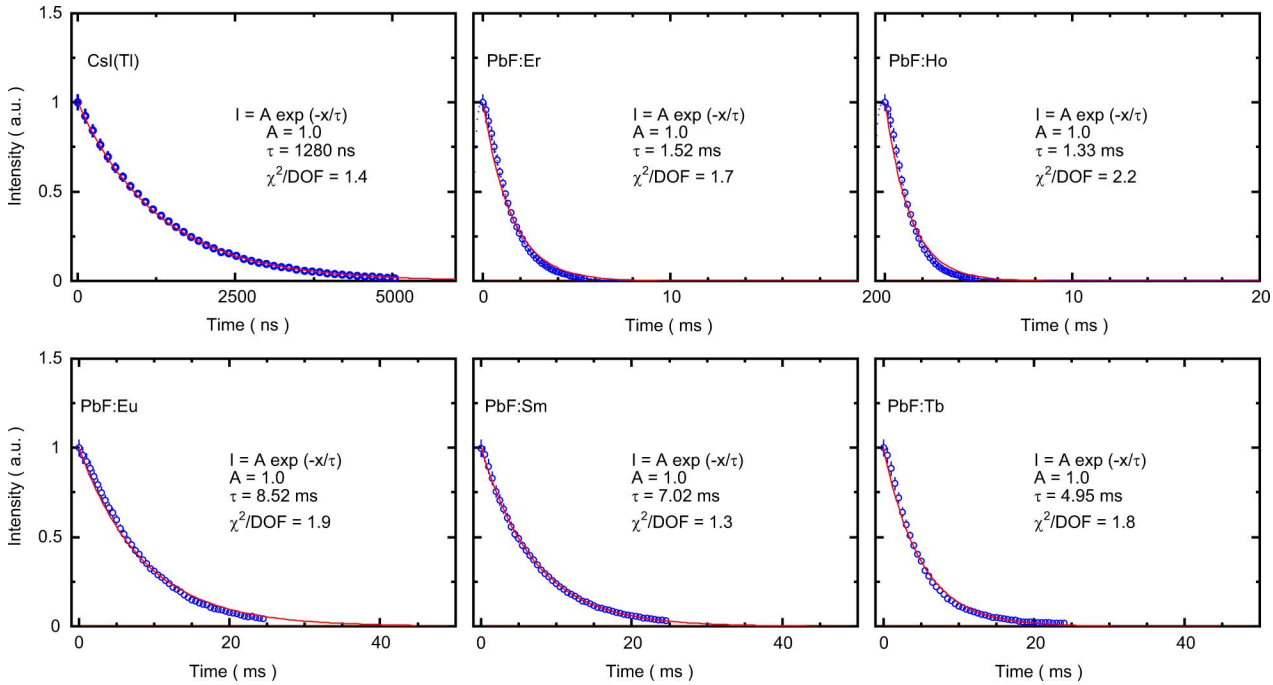

Fig. 5. The photo-luminescence pulse shape (blue circles), corresponding fit to an exponential (red lines) and the decay time constant are shown for the PbF_2 samples doped with Er, Ho, Eu, Sm and Tb as well as a reference CsI(Tl) sample.

TABLE I
DECAY TIME CONSTANT FOR DOPED LEAD FLUORIDE CRYSTALS.

Dopant	Er	Eu	Ho	Sm	Tb
Decay time constant (ms)	1.5	8.5	1.3	7.0	5.0

of PbF_2 samples doped with Pr and Gd are too weak to be useful to extract the decay time constant.

Table I summarizes the decay time constants for the PbF_2 samples doped with Er, Ho, Eu, Sm and Tb, which were found at a millisecond scale. These time constants are too long to be useful for high energy physics experiments.

IV. γ-RAY INDUCED ANODE PHOTO-CURRENT

Measurements of the absolute light yield by using the classical γ-ray pulse hight spectrum approach suffers from a large noise for doped PbF_2 samples with millisecond decay time. An alternative approach was taken to measure the DC anode photo-current induced by a γ-ray source at a fixed distance. The result of this measurement contains contributions from both the scintillation and the radiation induced phosphorescence. The latter, however, is negligible because of the weak source used and the small size of the PbF_2 samples. Fig. 6 shows the setup used for this measurement. A ^{137}Cs source of 57 μ-curie was used to excite the sample. A Hamamatsu R2059 PMT was used to measure the DC anode photo-current. The bias voltage of the PMT was fixed at 2,000 V, and the distance between the source and the samples was fixed at 2 cm as shown in the figure. The PMT anode current was measured by using a digital multi-meter before and after turning on the γ-ray source.

Fig. 7 shows histories of the anode photo-current measured for an undoped PbF_2 sample and a reference PWO sample which has a light output of 20 p.e./MeV. The anode photo-current after turning on the γ-ray source was found to be 42 nA and

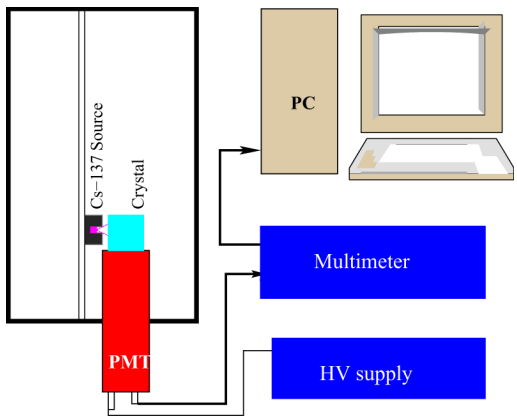

Fig. 6. The setup used to measure the γ-ray induced anode photo-current for PbF_2 samples. The distance between source and samples was fixed at 2 cm.

240 nA respectively for these two samples. The increase of the current for the undoped PbF_2 sample is caused by the contamination of various impurities in the raw material, which can be seen as the background. Fig. 8 shows the anode photo-current measured for all doped PbF_2 samples (solid dots and open circles) and the undoped PbF_2 sample (solid red square) when the source was turned on. A total of six doped PbF_2 samples showed an anode photo-current of larger than 50 nA. They are marked as the open circles in Fig. 8.

Table II lists their ID, dimension and dopant. By using the PWO sample as the reference, these numerical result indicates that the upper limit of their light output is 3 p.e./MeV. We also note that all six samples are featured with Eu doping, and were grown at Scintibow.

V. ^{137}Cs γ-RAY EXCITED PULSE HEIGHT SPECTRUM

The γ-ray induced anode current measurement has basically ruled out any significant γ-ray induced scintillation light in these

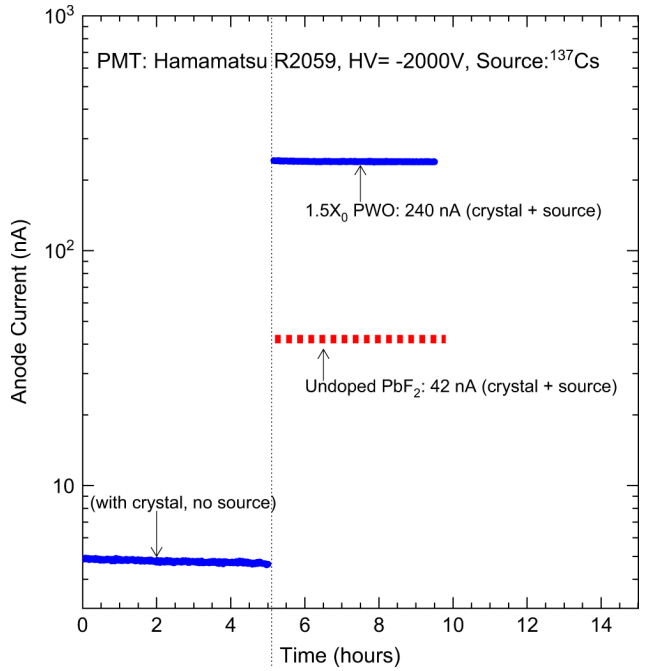

Fig. 7. The PMT anode current measured for an undoped PbF_2 sample (red dashes) and a reference small PWO sample (blue lines) with light output of 20 p.e./MeV.

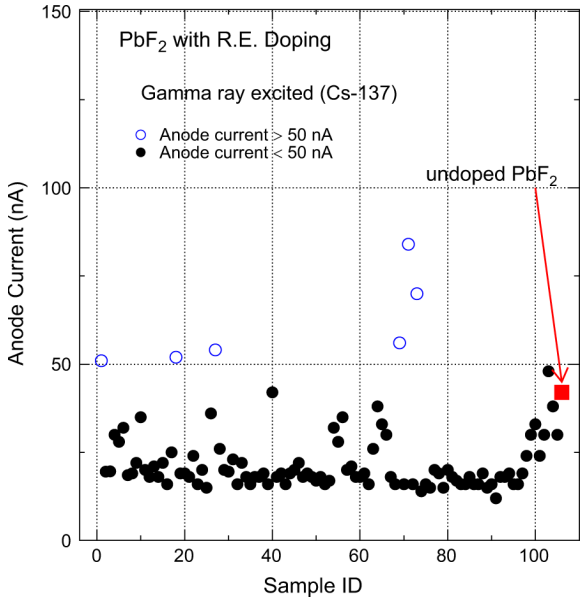

Fig. 8. The PMT anode photo-current measured for all doped PbF_2 samples (black solid dots and open circles) and the undoped PbF_2 sample (red solid square).

doped samples. To further confirm this observation and to look for any fast scintillation component with decay time of less than a few μs the ^{137}Cs γ-ray excited pulse height spectrum was measured for those doped PbF_2 samples listed in Table II. A Hamamatsu R2059 PMT was used as the readout device. Figs. 9 and 10 show the pulse height spectra (red solid lines) for samples Scintibow-1 and Scintibow-B21 respectively for an integration time of 1 μs. Also shown in these figures is the pulse height spectrum for an undoped PbF_2 sample (blue dashes). As expected that there is very little difference between spectra obtained from

TABLE II
THE PMT ANODE CURRENT FOR DOPED PbF_2 SAMPLES.

ID	Anode Current (nA)	Size (mm)	Doping
Scintibow-1	51	18 × 12 × 10	Eu
Scintibow-18	52	ϕ 22 × 15	Eu / Gd
Scintibow-27	53	ϕ 20 × 15	Eu / Tb
Scintibow-B19	56	ϕ 20 × 15	Eu / Tb / Na
Scintibow-B21	83	ϕ 22 × 15	Eu / Bi / Na
Scintibow-B23	73	ϕ 20 × 15	Eu / Bi / Na

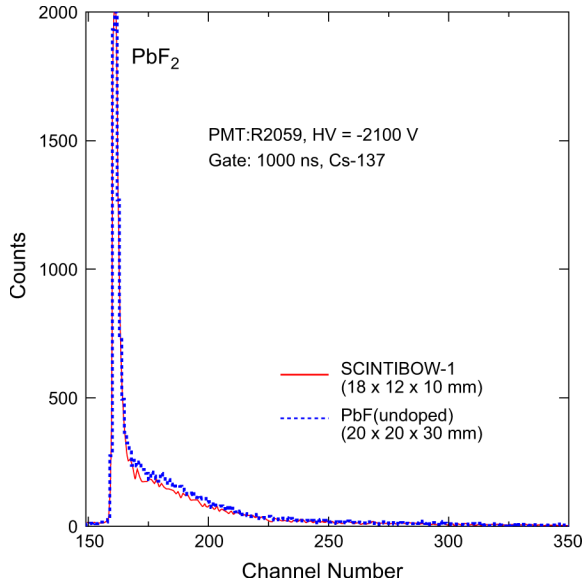

Fig. 9. ^{137}Cs γ-ray excited pulse height spectrum for doped PbF_2 samples Scintibow-1.

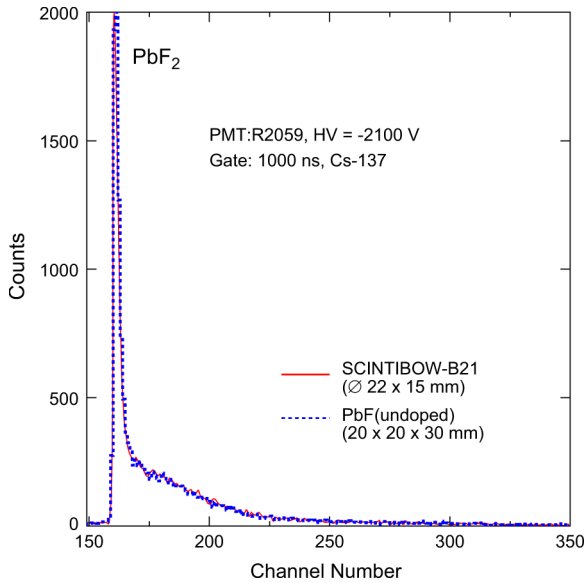

Fig. 10. ^{137}Cs γ-ray excited pulse height spectrum for doped PbF_2 samples Scintibow-B21.

the doped and the undoped PbF_2 samples, indicating that the amount of the luminescence light observed in the 1 μs gate is too weak to show a peak. The result obtained with an integration gate up to 10 μs is the same for all samples. This observation further confirmed the result obtained with the γ-ray induced anode current measurement described in the previous section.

VI. Summary

Because of its potential low cost, PbF_2 crystal is an attractive material for the HHCAL detector concept proposed for future high energy physics experiments. A search for scintillation was carried out in a set of doped cubic PbF_2 crystal samples. Consistent photo- and x-ray luminescence spectra were found in the PbF_2 samples doped with Er, Eu, Gd, Ho, Pr, Sm and Tb. The decay time of the Er, Eu, Ho, Sm and Tb doped samples was found to be at a millisecond scale as expected from the f-f transition of these rare earth elements [11]. While some Eu doped samples show γ-ray induced anode photo-current larger than the undoped sample the numerical result indicates that the scintillation light, if any, is less than 3 p.e./MeV measured by a PMT with bi-alkali photo-cathode. Their $^{137}\mathrm{Cs}$ γ-ray excited pulse height spectra measured with up to 10 μs integration gate were also found identical to that of the undoped sample, confirming that their luminescence is too weak to show a peak. Investigation will continue to search for scintillation in doped PbF_2 for the HHCAL detector concept. The work will concentrate on selective rare earth doping, other PbF_2 phases and mixtures [14].

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References

[1] A. Para, "High resolution jet calorimetry," in *International Linear Collider Workshop*, Chicago, 2008.

[2] N. Akchurin *et al.*, "Dual-readout calorimetry with a full-size BGO electromagnetic section," *Nucl. Instr. and Meth.*, vol. A610, pp. 488–501, 2009.

[3] R.-Y. Zhu, "Crystal calorimeters in the next decade," *Journal of Physics Series*, vol. 160, p. 012017, 2009.

[4] F. E. Maas *et al.*, E. Antonelli, Ed. *et al.*, "The PbF_2 calorimeter for the new parity violation experiment at MAMI," in *Proceedings of VI International Conference on Calorimetry in Particle Physics, Frascati Physics Series, 1996, and in Proceedings of Xth Pisa Meeting on Advanced Detectors*, 2006, pp. 669–678.

[5] C. Woody *et al.*, "A study on the use of lead fluoride for electromagnetic calorimetry," *IEEE Trans. Nucl.Sci.*, vol. 40, pp. 546–551, 1993.

[6] M. Nikl and K. Polak, "Luminescence kinetics of PbF_2 single crystals," *Phys. Stat. Sol. (a)*, vol. 117, pp. K89–K92, 1990.

[7] D. L. Alov and S. I. Rybchenko, "Luminescence of orthorhombic PbF_2," *J. Phys. Condens. Matter*, vol. 7, pp. 1475–1482, 1995.

[8] M. Itoh, H. Nakagawa, M. Kitaura, M. Fujita, and D. Alov, "Photoluminescence of orthorhombic and cubic PbF_2 single crystals," *J. Phys. Condens. Mater.*, vol. 11, pp. 3003–3011, 1999.

[9] S. E. Derenzo, W. W. Moses, J. L. Cahoon, R. C. C. Perera, and J. E. Litton, "Prospects for new inorganic scintillators," *IEEE Trans. Nucl. Sci.*, vol. 37, pp. 203–208, 1990.

[10] S. N. Baliakin *et al.*, "Deformation and thermal treatment application to heavy scintillators production," in *Heavy Scintillators for Scientific and Industrial Applications*, F. De Notaristefani, Ed. *et al.* Gif-sur-Yvette, France: Editions Frontieres, 1993, pp. 587–591.

[11] D. A. Anderson, J. A. Kierstead, P. Lecoq, S. Stoll, and C. L. Woody, "A search for scintillation in doped and orthorhombic lead fluoride," *Nucl. Instr. and Meth.*, vol. A290, pp. 437–476, 1994.

[12] D. Z. Shen, J. C. Liu, X. L. Yuan, Q. Deng, and Z. W. Yin, "X-ray excited emission spectra of PbF_2:Gd, Eu crystals," *Jour. Inor. Mater.*, vol. 10-1, pp. 11–16, 1995.

[13] C. L. Woody, S. P. Stoll, and J. A. Kierstead, "Observation of fast scintillation light in a PbF_2:Gd crystal," *IEEE Trans. Nucl. Sci.*, vol. 43, pp. 1303–1306, 1996.

[14] in *See, for Example, Presentations in the 2nd Workshop for Material Development for the HHCAL Detector Concept* , Beijing, May 9, 2010 [Online]. Available: http://indico.ihep.ac.cn/sessionDisplay.py?sessionId=2&slotId=0&confId=1470#2010-05-09