Scintillation properties of Gd doped β-PbF_2 crystal

SHEN Dingzhong (沈定中), REN Guohao (任国浩),
DENG Qun (邓 群), YIN Zhiwen (殷之文),
(Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201800, China)
C. Woody and S. Stoll
(Brookhaven National Lab, U.S.A.)

Received May 20, 1997

Abstract A single crystal sample of cubic lead fluoride doped with gadolinium (β-PbF_2:Gd) was prepared by use of the Bridgman-Stockbarger method. The crystal samples for testing with dimension of ø20 mm × 20 mm long were all polished. The dopant level of gadolinium is 0.15wt%. The light output and decay time of the samples were measured in the lab using ^{137}Cs source and 1 GeV test beam at AGS respectively. Experimental results indicated that β-PbF_2:Gd crystal produces a weak scintillation emission at room temperature corresponding to a light output of ~6 photoelectrons per MeV and most of the light is collected within a gate of 30 ns. There is no evidence of any significant slow component extending out of 1 μs. In the X-ray excited emission spectra of β-PbF_2:Gd at room temperature, two emission peaks, 277 nm and 312 nm, were found and corresponded to the transition of $^6I_J \rightarrow {}^8S_{7/2}$ and $^6P_J \rightarrow {}^8S_{7/2}$ of Gd^{3+} ions, respectively.

Keywords: β-PbF_2:Gd crystal, light output, decay time, emission spectrum.

Lead fluoride crystal exists in two forms: cubic phase (β-PbF_2) and orthorhombic phase (α-PbF_2). Usually, as-grown PbF_2 samples possess cubic symmetry. Since Dally and Hofstadter discovered that PbF_2 crystal could be used as Cherenkov radiator in 1968[1], more and more researchers have paid attention to the investigation of the luminescence of PbF_2 crystals. The most outstanding properties of PbF_2 are its high density of 7.77 g/cm^3 in the cubic phase (8.24 g/cm^3 in the orthorhombic phase), high average atomic number and short radiation length ($X_0 = 0.93$ cm). This crystal is nonhydroscopic, high transparent into the near ultraviolet. So it is expected that PbF_2 crystal can be used as a potential scintillator in electromagnetic calorimetry in the future. So far, the investigation showed that the luminescence of PbF_2 just exists at the liquid helium temperature. When the temperature increases to more than 40 K, it quenches quickly[2].

In order to make PbF_2 crystal scintillate at room temperature, a great deal of experiments have been carried out. In 1990, Derenzo et al. first discovered the scintillation of α-PbF_2 at room temperature when the excited α-PbF_2 powder using synchrotron X-radiation[3]. Baliakin et al. explained the luminescence quenching of cubic lead fluoride crystal at room temperature by high fluorine ion mobility and proposed that the luminescence intensity of α-PbF_2 crystals would be superior to that of β-PbF_2 and began to study the transformation from β-PbF_2 to α-PbF_2. By means of hot, mechanical pressing, they successfully obtained a sample in which the concentration of α-PbF_2 was less than 5% near the edge of the sample to about 30% at the center. This sample demonstrated the room temperature fluorescence and scintillation. The emission spectrum extended from 350 to 550 nm, and decay time ranged from less than 15 to 30 ns. The light output was

increasing with the increasing of the amount of orthorhombic phase[4]. Unfortunately, Anderson et al. did not find the phenomena similar to Baliakin's when they carried out a similar experiment, even though the concentration of α-PbF_2 in their sample was as high as 99%[5]. The light outputs observed from these samples were too weak to distinguish whether they are scintillation activity or Cherenkov light.

The alternative way to search for the scintillation of lead fluoride at room temperature is by doping. A lot of rare earth elements have been introduced into the PbF_2 crystal lattice. But so far, no scintillation signal above the level of Cherenkov emission has been detected when excited with different radioactive sources.

The sample studied here was β-PbF_2 crystal doped with gadolinium. It is expected that the addition of a small amount of gadolinium will produce scintillation emission with a fairly short decay time.

1 Crystal growth

The raw material used was α-PbF_2 powder prepared by special techniques and its purity was 99.99%. A deoxidant named 703[6] was doped into the batch for removing the oxygen from the system. Gadolinium element was added to the α-PbF_2 powder in the form of gadolinium fluoride. The dopant level was 0.15wt%. The α-PbF_2 powder, deoxidant and gadolinium fluoride were mixed together homogeneously and then put into a platinum crucible. The crystals were grown by means of the traditional non-vacuum Bridgman-Stockbarger method. After the furnace temperature reached 1 040℃, the mixed batch was kept at this temperature for a few hours, then descended at a growth rate of 1.6 mm/h, and the temperature gradient was always kept between 25 and 30℃/cm. The temperatures of the furnace and crucibles were monitored and controlled by a temperature controlling system JWT-702. The whole growing process was carried out in a closed environment. After annealing, the crystals were cut and polished into ø20 mm × 20 mm long samples for further experiments.

2 Experimental results and discussion

2.1 γ-Ray energy spectroscopy

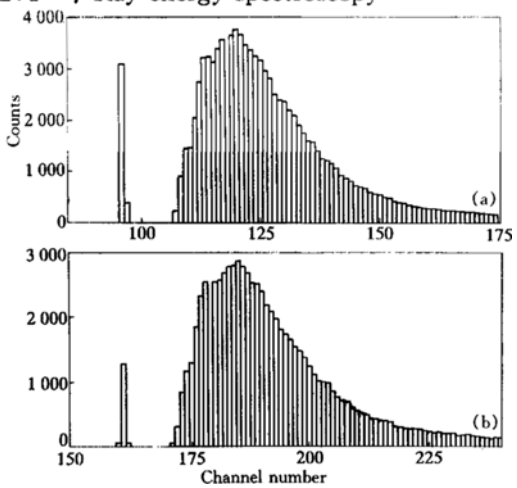

Fig. 1. The pulse height spectra of β-PbF_2 : 0.15% Gd crystal excited by γ-ray (^{137}Cs source).

^{137}Cs was used as the excitation source. The light output of the sample was measured using a Hamamatsu R2059 2″ diameter quartz window photomultiplier tube. The sample was wrapped (only one end was left for light out) in white reflecting teflon and coupled to the phototube using a UV transparent optical grease. The phototube was operated at a voltage of 2.5 kV at which the gain corresponded to ~ 6 channels per photoelectron. Fig. 1 shows the pulse height spectra obtained with a 50 ns and 1 μs gate, respectively. It demonstrates that the channel difference between the pulse peak of the sample and the pedestal is 24.5 ch. Thus, the light yield of PbF_2 : Gd crystal can be obtained

as follows:

$$(24.5\text{ch} \div 6\text{ch/p.e.})/0.662\text{MeV} \approx 6.2\text{p.e./MeV}.$$

Figure 2 shows the relationship between the light yield for Gd doped crystal and the integration time. It indicates that the light yield rises with the increase of the integration time when the time gate is less than 30 ns and reaches to a maximum at 30 ns and then levels off. It is essentially independent of gate length beyond about 30 ns. This means that there is no significant slow component in the light output.

2.2 Beam tests

The crystal was again wrapped in teflon and coupled to a Hamamatsu R1398 1-1/8″ UV glass window phototube with optical grease and placed in 1 GeV test beam at the AGS of Brookhaven. The beam consisted of a mixture of pions, protons and electrons and was defined by a 1 cm^2 scintillator in front of the crystal. Due to the fact that the crystal was so small, electron showers in the crystal were very poorly contained and only minimum ionizing particles could be used to obtain useful information on the light output. Fig. 3 shows the pulse height spectrum for the minimum ionizing peak along with the pedestal using a QVT, a sensitivity of 1 pC/channel and a 200 ns gate. The peak in the figure corresponds to ~70 channels and the pedestal to 12.3 channels. The difference corresponds to $70 - 12.3 = 57.7$ ch. Since the sensitivity of the instrument is 1 pC/ch ($1\text{ pC} = 10^{-12}\text{C}$, $1\text{ e} = 1.602\,19 \times 10^{-19}\text{C}$), the electron numbers correspond to

$$\frac{57.7\text{ch} \times 10^{-12}\text{C/ch}}{1.602\,19 \times 10^{-19}\text{C/e}} = 3.6 \times 10^8 \text{ electrons}.$$

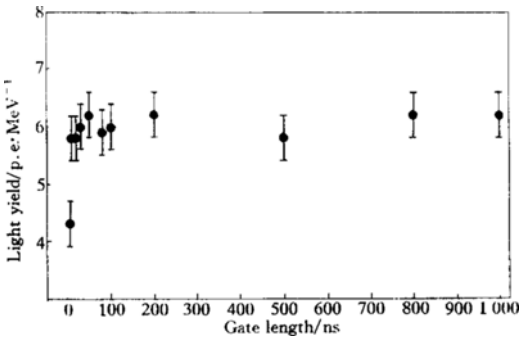

Fig. 2. Light output of β-PbF_2 : 0.15% Gd crystal as a function of integration time.

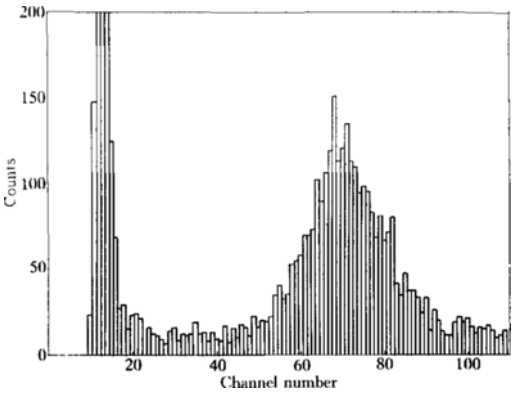

Fig. 3. Pulse height spectrum of β-PbF_2:Gd crystal under the excitation of 1 GeV test beam.

The phototube was operated at a voltage of 1 300V with a gain of 2.9×10^6. This implies that the minimum ionizing peak corresponds to $3.6 \times 10^8/2.9 \times 10^6 = 124$(p.e.). Given that the energy loss in the sample is ~9.6 MeV/cm, the total energy loss corresponding to the minimum ionizing peak is ~9.6 MeV/cm × 2 cm = 19.2 MeV. This would imply a photoelectron yield of

$$124\text{p.e.}/19.2\text{MeV} = 6.5\text{ p.e./MeV}.$$

This value agrees very well with the 6.2 p.e./MeV measured with the ^{137}Cs source. It is clear that the light output of PbF_2:Gd crystal is stable. If we consider the leakage of the shower out of the sides as well as the rear of the crystal, the real light yield would be more than the present value. Compared with the light yield of the un-doped PbF_2 crystal (970—1 200 p.e./GeV)[7], the

light yield of β-PbF_2 : Gd crystal is approximately a factor of 6 higher than that of un-doped PbF_2. This proves that Gd^{3+} ion is an activator and plays the role of a luminescence center in the β-PbF_2 crystals.

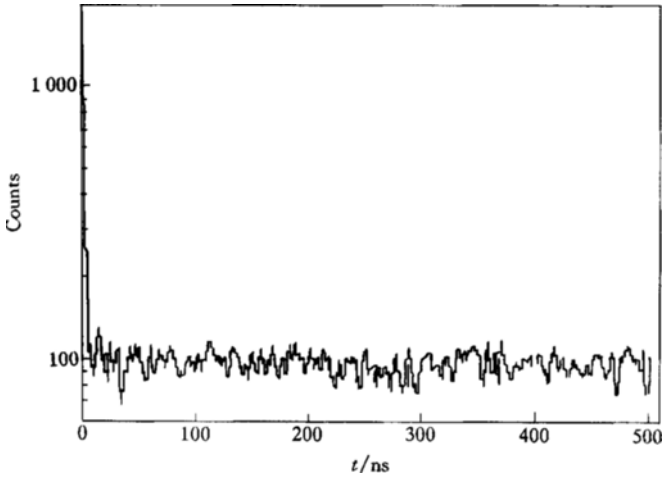

Fig. 4. Decay time spectrum measured for Gd-doped PbF_2 crystal.

As shown in fig. 4, the decay time curve of Gd-doped PbF_2 crystal was also measured using single photon counting technique. The decay time corresponding to fig. 4 is less than 20 ns and there is no significant signal at longer times out of 500 ns. This result agrees very well with that measured in fig. 2; that is, there is no indication of any significant slow component beyond about 50 ns in the light output of Gd-doped PbF_2 crystal.

2.3 Transmission spectra

Transmission and band-edge are very important parameters indicating the properties of scintillation crystals. Fig. 5 gives the optical transmission spectrum measured along the longitudinal axis of the sample. One can see from the curve that the transmission and band-edge of β-PbF_2 : Gd are 80% and 250 nm respectively. There are not any other discernible absorption bands except a weak absorption at 270 nm due to small amount of impurities. The data indicate that β-PbF_2 : Gd crystal is a clear optical material with a transmission extending to UV.

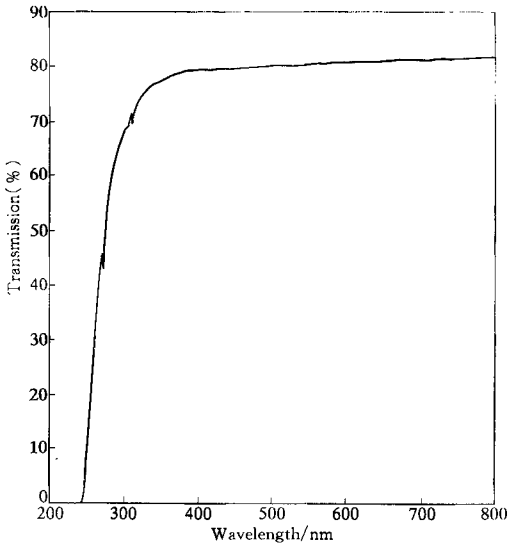

Fig. 5. Transmission spectrum of β-PbF_2 : Gd crystal.

2.4 Emission spectra excited by X-ray

X-ray (W target) was used as a source to excite β-PbF_2 : Gd crystal. The X-ray tube was operated at a voltage of 80 kV. The recording wavelength ranged from 200 nm to 1 μm, and the current from 0 to 5 mA. Whole testing work was carried out at room temperature. Fig. 6 shows the emission spectra of β-PbF_2 : Gd crystal excited by X-ray. There are two emission peaks in the spectra: one peak's wavelength is 312 nm, the relative intensity is 59% and FWHM is 6.0 nm; the other peak's wavelength is 277 nm, and its relative intensity is 16%, FWHM is 7.5 nm. It was reported that there were three main emission bands in cubic un-doped PbF_2 crystal at liquid helium temperature: at 285, 303 and 525 nm respectively. All of these three emission bands will be quenched at room temperature[2]. The 303 nm emission in un-doped β-PbF_2 can be interpreted by the transition $^3P_1 \rightarrow {}^1S_0$ in Pb^{2+} ion. The bands at 285 and 525 nm can be also ascribed to Pb^{2+} essentially. They are caused by the distor-

tion of the neighboring Pb^{2+} ions by some intrinsic defect or various ionic impurities embedded in the crystal during the growth process. But the above three intrinsic emission bands were not found in the X-ray excited emission spectra of β-PbF_2 : Gd crystal. On the other hand, the decay times of the emission bands at 285, 303 and 525 nm of un-doped cubic PbF_2 crystal at liquid helium temperature were 80, 214 and 610 μs respectively; that means, all of them are slow components[2]. However the emission of β-PbF_2 : Gd crystal at room temperature is fast components. These facts show that there is no direct connection between the emission 312 and 277 nm of β-PbF_2 : Gd crystal and its crystal lattice or intrinsic defects. The emission of β-PbF_2 : Gd crystal is only related with the transition of different energy levels in dopant Gd^{3+} ions.

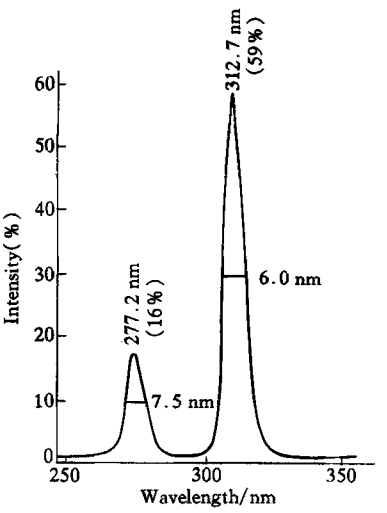

Fig. 6. Emission spectrum of β-PbF_2 : Gd crystal excited by X-ray at room temperature.

According to the investigation on the spectroscopy of rare earth elements[8,9], Gd^{3+} ion ($4f^7$) has an $^8S_{7/2}$ ground state and several excited levels: ^6P_J, ^6I_J, ^6D_J and ^6G_J. Under the excitation of short wave length ultraviolet radiation, the transition from $^6P_J \rightarrow {}^8S_{7/2}$ will emit a characteristic narrow emission at 312 nm. And the transition from $^6I_J \rightarrow {}^8S_{7/2}$ corresponds to the emission at 277 nm. In the emission spectra of β-PbF_2 : Gd crystal, the intensity of 312 nm is stronger than that of 277 nm. This could be explained by the fact that since ^6P_J levels are superior to ^6I_J levels, they are easily occupied by electrons during excitation. The Gd^{3+} emission intensity depends on the concentration of Gd^{3+} ions in the crystal. However, the emissions from the transition of $^6D_J \rightarrow {}^8S_{7/2}$ and $^6G_J \rightarrow {}^8S_{7/2}$ were not found. This may be explained by the re-absorption in the crystal. Since the band edge of β-PbF_2 : Gd crystal is 250 nm (fig. 5), and the emission wavelengths of the transition $^6D_J \rightarrow {}^8S_{7/2}$ and $^6G_J \rightarrow {}^8S_{7/2}$ are 254 ($^6D_{9/2}$), 217 and 206 nm[9], it is difficult for them to transmit through the crystal.

3 Conclusions

The light output and decay time of β-PbF_2 : Gd crystal were measured using ^{137}Cs radioactive source and 1 GeV test beam at AGS. The test results indicate that this material produces a weak scintillation emission corresponding to a light output of ~6 photoelectrons per MeV. Most of the light is collected within a gate of 30 ns and there is no evidence of any significant slow component extending out of 1 μs. In the emission spectra excited by X-ray, there are two strong emission peaks: 312 and 277 nm. The emission at 312 nm is ascribed to the transition from $^6P_J \rightarrow {}^8S_{7/2}$ and the emission at 277 nm is ascribed to the transition from $^6I_J \rightarrow {}^8S_{7/2}$. The emission intensity of β-PbF_2 : Gd crystal depends on the concentration of Gd^{3+} in the crystal. These results demonstrate that Gd^{3+} ions are activators and play a role of an independent luminescence center in the β-PbF_2 : Gd crystal. So far, the light output of β-PbF_2 : Gd crystal is still too low to be used as a scintillator. Nevertheless, the appearance of scintillation of β-PbF_2 : Gd crystal at room temperature has opened up a new research field for the scintillation crystals.

References

1 Dally, E. B., Hofstadter, R., High energy γ-ray detector with good resolution, *Rev. Sci. Instru.*, 1968, A10: 658.

2 Nikl, M., Polak, K., Luminescence kinetics of PbF_2 single crystals, *Phys. Status Solid*, 1990, A117: k89.

3 Derenzo, S. E., Moses, W. W., Cahoon, J. L. et al., Prospects for new inorganic scintillators, *IEEE Trans. Nucl. Sci.*, 1990, 37: 203.

4 Baliakin, S. N., Egorov, V. K., Klassen, N. V. et al., Deformation and thermal treatment application to heavy scintillators production, crystal 2000, *Int. Conf. on Heavy Scintillators for Scientific and Industrial Applications, Chamonix, France, Sept.* 22—26, 1992, 587—591.

5 Anderson, D. F., Kierstead, J. A., Woody, C. L. et al., A search for scintillation in doped and orthorhombic lead fluoride, *Nucl. Instr. Meth. Phy. Res.*, 1994, A342: 473.

6 Shen Dingzhong, Yuan Xianglong, Zhang Lixing et al., Large size crystal growth for beta-lead fluoride, *Journal of the Chinese Ceramic Society* (in Chinese), 1995, 23(6): 667.

7 Anderson, D. F., Kobayashi, M., Woody, C. L. et al., Lead fluoride: An ultra-compact Cherenkov radiator for EM calorimetry, *Nucl. Instr. Meth. Phy. Res.*, 1990, A290: 385.

8 Shen Dingzhong, Liu Jiancheng, Yuan Xianglong et al., X-ray excited emission spectra of P_6F_2:Gd, Eu crystals, *Journal of Inorganic Materials* (in Chinese), 1996, 10(1): 11.

9 Kirikova, N. Yu., Klimenko, V. E., Makhov, N., Luminescence properties of rare earth trifluorides, *Inorganic Scintillators and Their Applications, Scint* 95, *Delft, the Netherlands*, Aug. 28—Sept. 1, 1995, 196—199.