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INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS

J. Phys. D: Appl. Phys. **37** (2004) 938–941 PII: S0022-3727(04)72707-2

A high-density inorganic scintillator: lead fluoride chloride

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Received 28 November 2003
Published 24 February 2004
Online at stacks.iop.org/JPhysD/37/938 (DOI: 10.1088/0022-3727/37/6/020)

Abstract

Lead fluoride chloride (PbFCl) crystal, whose density is about 7.11 g cm^{-3}, was grown by the modified Bridgman method. PbFCl can emit violet-blue light with the peaks at 392 and 420 nm when excited by ultraviolet light or x-rays. The light yield of PbFCl under irradiation of ^{137}Cs is about 20% as that of bismuth germanate. A fast and a slow decay time with 4 ns and 35 ns, respectively, were obtained when PbFCl was studied with a pulsed x-ray facility. The irradiation resistivity of PbFCl was studied by applying ^{60}Co. The results of the experiments indicate that PbFCl is a new inorganic scintillator.

1. Introduction

A large variety of inorganic scintillators have been widely used in x-ray computed tomography (X-CT), positron emission tomography (PET), security examination and high-energy physics experiments [1]. One of the characteristic features of these scintillation crystals is that they belong to an inorganic compound that has a high density, leading to a large absorption coefficient for radiation. Lead fluoride chloride (PbFCl) has a high density (7.11 g cm^{-3}) and effective atomic number. Its scintillation properties have not been reported until now. Argonne Institution, USA, has been asked to look into a detector containing 500 tons lead perchlorate solution for a neutrino telescope for observing galactic supernovae. Lead perchlorate is carcinogenic, poisonous, corrosive, acidic and explosive, and so it is difficult to handle in an experiment. PbFCl has lead and chlorine, and has high density. If PbFCl can be used as a scintillator, it has many advantages over lead perchlorate solution for the neutrino detector. PbFCl powder was first synthesized in 1911 from a solution [2]. Much attention has been given to its reflectance [3, 4], ionic conductivity [5–7], photoluminescence [8, 9], etc. PbFCl has a tetragonal layered structure. It will cleave easily along the (001) plane, making growth into a large ingot difficult. Small pieces of PbFCl crystal can be grown by the zone refining method, but the process is complex and the conditions of growth are difficult to control [5, 10]. In our experiment, large PbFCl planar single crystals were obtained by the modified Bridgman method [11]. A transparent plate of size 13 × 7 × 4 mm^3 of PbFCl was selected as the specimen for this study.

In this paper, the photoluminescence, radioluminescence, light yield and decay time of PbFCl at room temperature and its irradiation resistivity were studied. The results indicate that PbFCl has good scintillation properties.

2. Experiments and discussion

2.1. Transmittance

The transmittance spectrum of the sample along the [001] direction was measured using a Shimadu UV-2501 spectrophotometer. The result is shown in figure 1. The absorption edge of PbFCl is about 270 nm. No obvious absorption band is found from 270 to 800 nm. The absorption near 381 nm found in PbFCl crystals has been attributed to either oxide impurities or a nonequimolar composition [3]. Our experiments show that an excess of PbF_2 or $PbCl_2$ does not introduce a new absorption band [12]. So the absorption near 381 nm is caused by the existence of an oxide impurity.

2.2. Photoluminescence

The photoluminescence of PbFCl at low temperatures was studied in detail in 1976 [8, 9]. The temperature dependence

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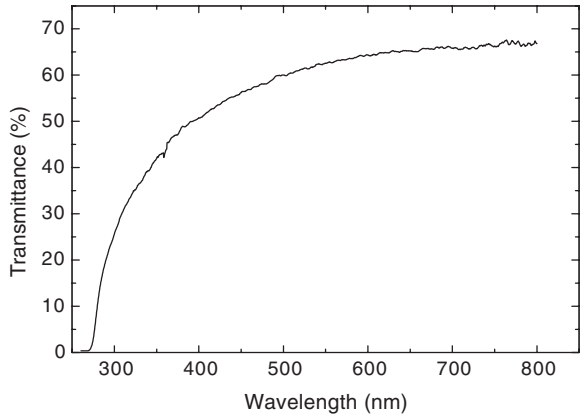

Figure 1. Transmittance of PbFCl crystal along the [001] direction (in 4 mm thickness).

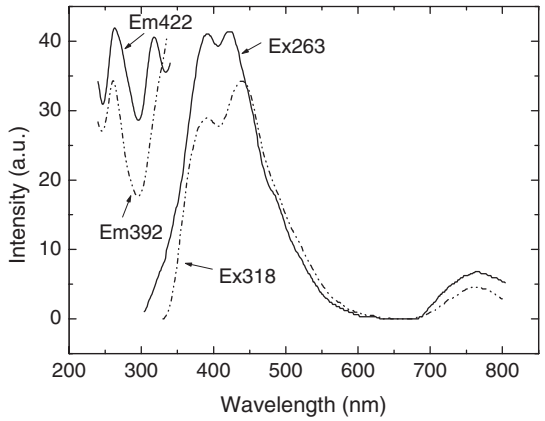

Figure 2. Excitation and emission spectra of PbFCl ($T = 300$ K).

of the intensities of the emissions of PbFCl indicated that the emissions were quenched above 175 K. It was reported that oxygen could greatly degrade the transmittance of halide crystals such as PbF_2, BaF_2 and CeF_3 [13–15]. The intensity of the luminescence of halide crystals will be decreased by oxygen contamination since some of the emitted light will be absorbed by the host materials. Our experiments showed that PbFCl crystals still have strong violet and blue emissions at room temperature if oxygen contamination can be avoided effectively [11]. In this paper, the photoluminescence of the sample was measured using a fluorescence spectrophotometer (Perkin Elmer, LS55B) at room temperature ($T = 300$ K). A slit width of 7 nm was selected for the whole process of measurement. A 350 nm filter was used in the measurement of the emission spectra. The results are shown in figure 2. When PbFCl was excited by 263 nm ultraviolet light, a violet emission, a blue emission and a weak red emission were observed, with the peaks at 392 nm, 422 nm and 760 nm, respectively. The violet and blue emission bands are ascribed to a transition of a Pb^{2+} ion in the presence of a defect centre. The red emission band is due to the formation of Pb^{+} centres during and after ultraviolet irradiation [9].

2.3. X-ray excited luminescence

An accurate knowledge of PbFCl emission is important. Besides photoluminescence, x-ray excited luminescence

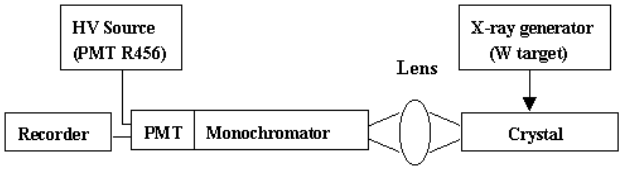

Figure 3. Scheme of the set-up for measuring the XEL spectrum.

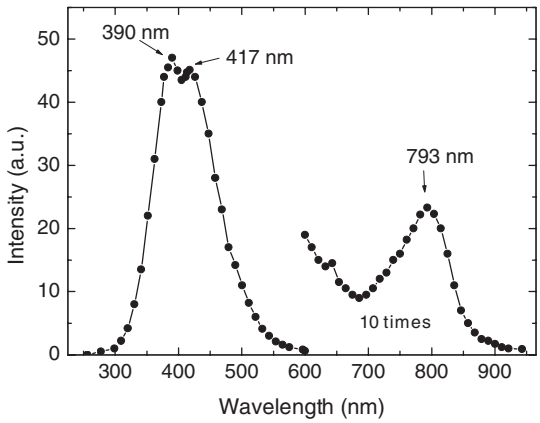

Figure 4. XEL spectrum of PbFCl crystal ($T = 300$ K).

(XEL) was also measured at room temperature. The instrument was designed and constructed at the Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS). The scheme of the set-up is given in figure 3. Its working condition is 50 kV, 4 mA and W target. The sample was wrapped with Teflon tape except a large face for letting the emission light out of the sample. The light was detected by a photomultplier tube (R456). The luminescence spectra were recorded by an x–y recorder.

From XEL spectra (figure 4) we can see that PbFCl also gives out a violet emission and a blue emission with the peaks at 390 nm and 417 nm, respectively, when a PbFCl crystal is excited by x-rays. The two emission bands are close to those of photoluminescence spectra. The red emission is so weak that it can be hardly seen in the XEL spectrum. Upon increasing the intensity of the spectrum from 600 to 940 nm by ten times, the red emission with the peak at 793 nm was then clearly seen, shifting 30 nm towards a longer wavelength compared with that of photoluminescence spectra. From the discussion above, we can conclude that PbFCl has luminescence at room temperature.

2.4. Light yield

It is difficult to get the absolute light yield of a new scintillator directly. In order to evaluate the light yield of a PbFCl crystal, the sample was compared in response to 662 keV photons with a bismuth germanate (BGO) crystal under the same conditions. The measurement was carried out at room temperature. The PbFCl crystal was wrapped on five sides with a Teflon tape and then optically coupled to a quartz-windowed XP2262B photomultiplier tube (PMT) with silicone oil. The crystal was irradiated with 662 keV photons from a ^{137}Cs source, and the light was collected with 1 μs shaping time. The resulting pulse height spectrum is plotted as in figure 5. An obvious photo peak

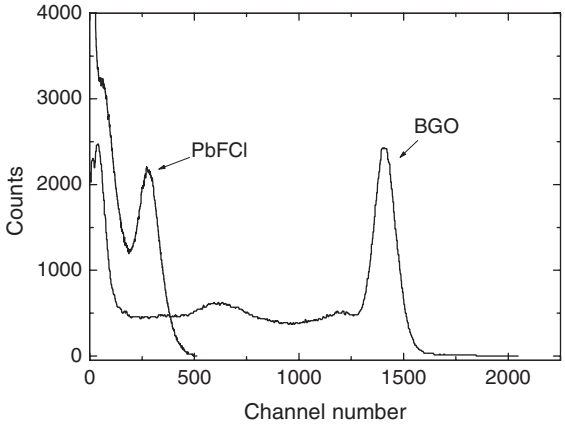

Figure 5. Pulse height spectra of PbFCl and BGO crystals ($T = 300$ K).

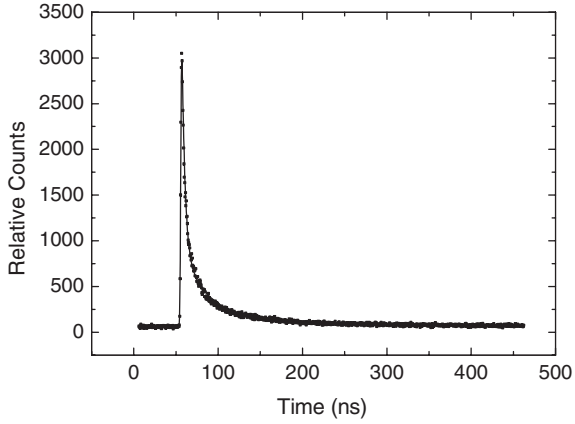

Figure 6. Decay time spectrum obtained for PbFCl ($T = 300$ K).

is seen with channel number 278. Then the PbFCl crystal was removed and the same test was performed on a same-size BGO crystal. The channel number of the peak is about 1408. So the relative light yield of PbFCl is approximately 20% that of BGO. Many efforts have been made to improve the light yield of $PbWO_4$ crystals recently [16, 17]. If the light yield of $PbWO_4$ could be improved to more than 5% of that of BGO, $PbWO_4$ can be successfully used in PET by using bialkali PMTs, not photodiodes (PDs) or multi-alkali PMTs, as light detectors [18]. So the light yield of PbFCl is not high enough, but it can meet this application requirement in PET.

2.5. Decay time

The decay time was measured with the pulsed x-ray facility described in detail by Derenzo [19]. Light from a pulsed laser diode incident on a photocathode generates a pulse of electrons that are accelerated and bombard a tungsten anode, producing a 30 keV x-ray pulse. The pulsed x-ray was used to excite the PbFCl crystal, and an XP2020Q PMT was used to collect the signal. The result of this measurement is shown in figure 6. To an approximation, the decay time can be derived by two exponential components fit to the decay data. A fast and a slow decay time of 4 ns and 35 ns, respectively, were obtained. The ratio of the light intensity of the fast component and the slow component is about 3–7. The decay time of PbFCl is much faster than that of BGO.

2.6. Radiation resistivity

A PbFCl crystal of 1 mm thickness was irradiated by a ^{60}Co γ-ray source at two different absorbed energy doses. The sample was fixed with its (001) plane perpendicular to the direction of the γ-quanta of the source. The variation in the irradiation effect has been investigated by measuring the transmittance. The transmittance spectra before and after irradiation of the sample are displayed in figure 7. After irradiating the sample for 28 h at a rate of 35 rad h^{-1}, a very small transmission loss is observed in the spectrum. When irradiation is carried out for 48 h at a rate about 500 rad h^{-1}, the sample turns a little black and the radiation damage is clearly seen in the spectrum. The loss of transmittance reaches 11.54% at a wavelength of 422 nm. The optical bleaching of damaged

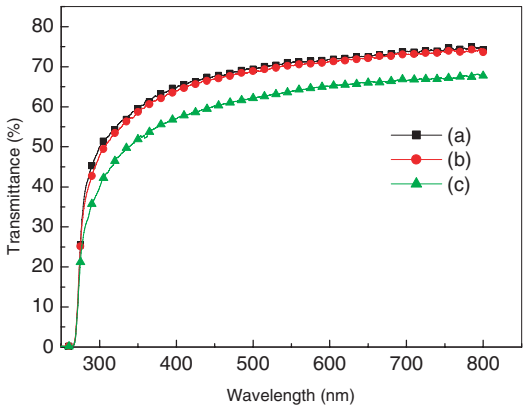

Figure 7. Transmittance curves of PbFCl crystal in 1 mm thickness along the [001] direction: (a) before irradiation, (b) after 35 rad h^{-1} × 28 h, (c) after about 500 rad h^{-1} × 48 h.

Table 1. Characteristics of PbFCl in comparison with some inorganic scintillators.

	BaF_2	BGO	$PbWO_4$	NaI(Tl)	PbFCl
Density (g cm^{-3})	4.9	7.13	8.3	3.67	7.11
Melt point (°C)	1280	1050	1123	651	601
Decay time (ns)	0.6 620	300	15	230	4 35
Peak emission (nm)	220 310	480	420	415	392 420
Light yield (%NaI(Tl))	5–16	10	0.4	100	2.0

crystals has been studied in PbF_2 and BaF_2 crystals [20, 21]. The phenomenon is also observed in PbFCl crystals and will be studied in the future.

3. Conclusions

The measurements on the scintillation properties of PbFCl at room temperature demonstrate that PbFCl is a new inorganic scintillator. The scintillation properties of PbFCl are listed in table 1 compared with those of BaF_2, BGO, $PbWO_4$ and NaI(Tl). Its density is 7.11 g cm^{-3}, close to that of BGO. The violet and blue emissions with the peaks at 392 and 420 nm are coupled well to PMT. The light yield of PbFCl is about 20% that

of BGO. A decay time of 4 and 35 ns is very fast among typical inorganic scintillators. The combination of high density, fast decay time, reasonable light yield, low melting point and cheap raw materials suggests that PbFCl would be useful for practical applications, especially in neutrino detectors. To produce large and high-quality PbFCl crystals, improving the crystal growth technique is presently being investigated.

Acknowledgments

The authors thank Prof. M Gu (Tongti University, China) and his colleagues for measuring the decay constant of PbFCl.

References

[1] van Eijk C W E 2001 *Nucl. Instrum. Methods* A **460** 1
[2] Starck G 1911 *Z. Anorg. Allg. Chem.* **70** 173
[3] Eijkelenkamp A J H 1976 *Phys. Status Solidi* b **76** 153
[4] Eijkelenkamp A J H and Vos K 1976 *Phys. Status Solidi* b **76** 769
[5] Schoonman J, Dirksen G J and Blasse G 1973 *J. Solid State Chem.* **7** 245
[6] Halff A F and Blasse G 1973 *Solid State Commun.* **13** 677
[7] Halff A F 1979 *J. Solid State Chem.* **27** 397
[8] Eijkelenkamp A J H 1976 *J. Solid State Chem.* **19** 313
[9] Eijkelenkamp A J H 1976 *Solid State Commun.* **18** 295
[10] Corsmit A F and Dirksen G J 1977 *J. Cryst. Growth* **37** 187
[11] Chen J M *et al* 2003 *J. Cryst. Growth* **250** 393
[12] Chen J M *et al* 2004 *J. Cryst. Growth* at press
[13] Ren G H *et al* 2003 *J. Cryst. Growth* **247** 141
[14] Sabharwal S C *et al* 2002 *J. Cryst. Growth* **240** 473
[15] Gao M *et al* 1994 *Nucl. Instrum. Methods* A **348** 163
[16] Kobayashia M *et al* 2002 *Nucl. Instrum. Methods* A **486** 170
[17] Mao R H *et al* 2002 *Nucl. Instrum. Methods* A **486** 196
[18] Annenkov A *et al* 2000 *Nucl. Instrum. Methods* A **450** 71
[19] Derenzo S E 1994 *IEEE Trans. Nucl. Sci.* **41** 629
[20] Achenbach P *et al* 1998 *Nucl. Instrum. Methods* A **416** 357
[21] Ma D A, Zhu R Y and Newman H 1995 *Nucl. Instrum. Methods* A **356** 309–18