

Doped Lead Fluoride Chloride Crystals for the HHCAL Detector Concept

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Abstract—We report an investigation on pure and doped PbFCl crystals. Optical and scintillation properties, such as emission and transmittance spectra, light output and decay kinetics, were measured at different temperatures. Three emission bands at 2.27, 2.85 and 3.39 eV are observed at 77 K. Thermal quenching effect is also observed. While a scintillation component peaked at 400 nm with 3 ns decay time is observed in all PbFCl samples, a secondary emission at 550 nm with 360 ns decay time is found in the K doped PbFCl samples. The origins of three emission bands and further development of PbFCl for the HHCAL detector concept are discussed.

Index Terms—Calorimeter, crystal, emission, light output, scintillator, thermal quenching.

I. INTRODUCTION

AIMING at the best jet-mass resolution, inorganic crystal scintillators are being investigated for a homogeneous hadronic calorimetry (HHCAL) detector concept with dual readout for both Cherenkov and scintillation light for future high energy lepton colliders [1], [2]. Fig. 1 shows a schematic of a typical HHCAL cell with a pointing geometry [3]. Because of the unprecedented volume (70 to 100 m³) foreseen for the HHCAL detector concept the materials must be 1) dense (to minimize the leakage and 2) cost-effective. They should also be UV transparent (for effective collection of the Cherenkov light) and allow for a clear discrimination between the Cherenkov and scintillation light. The preferred scintillation light is thus at a longer wavelength, and not necessarily bright nor fast. Inorganic crystals being investigated are lead fluoride (PbF₂), lead fluoride chloride (PbFCl) and BSO [4]. Because of its high density (7.11 g/cm³), low UV cutoff wavelength (280 nm), low melting point (608 °C) and low raw material cost, PbFCl crystals are under development at the Shanghai Institute of Ceramics (SIC) for the HHCAL detector concept.

Fig. 2 shows the lattice structure of PbFCl crystal. It has a tetragonal layered structure (space group P4/nmm), which consists of two adjacent planes of chloride ions perpendicular to the *c*-axis, leading to a cleavage plane along (001) [5]. This

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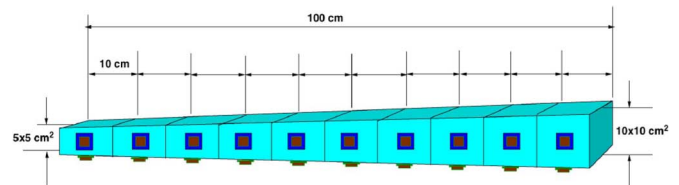


Fig. 1. Schematic showing a typical cell for the HHCAL detector concept.

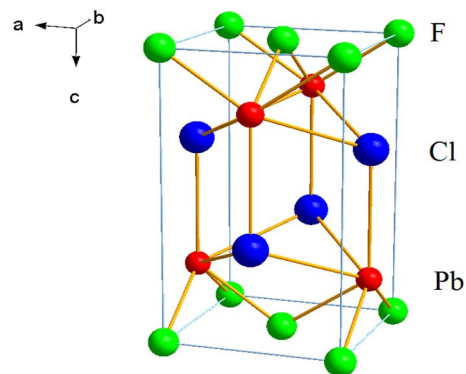


Fig. 2. Lattice structure of PbFCl crystal.

cleavage plane is one of the obstacles preventing PbFCl to be grown in large size.

II. LEAD FLUORIDE CHLORIDE CRYSTAL GROWTH

Fig. 3 shows photographs of the pure and doped PbFCl samples grown by the modified Bridgman method [6]. The raw materials of PbFCl compound were prepared by mixing PbF₂ and PbCl₂ powders of 4N purity. The ratio of PbF₂/PbCl₂ was less than one since Cl is easier to evaporate as compared to F [7]. A deoxidizer was also mixed in the raw materials. The mixtures were charged and sealed in Pt crucibles without seeds. The temperature of the resistance heated furnace was set to 630 °C and was controlled to a precision of ±1 °C. The longitudinal temperature gradient near the growth interface was 30 °C/cm to 40 °C/cm. The lowering speed of the crucible was 1 to 10 mm/day. After the growth, the crystals were cooled to the room temperature at a rate of 30 °C/h. The entire growth process was carried out in air atmosphere.

III. EXPERIMENTAL RESULTS

For the X-ray excited luminescence (XEL) measurements, samples were placed in the sample compartment of a HITACHI F-4500 spectrophotometer. X-rays generated by an Amptek E3-T X-ray tube were used to excite the sample through a small

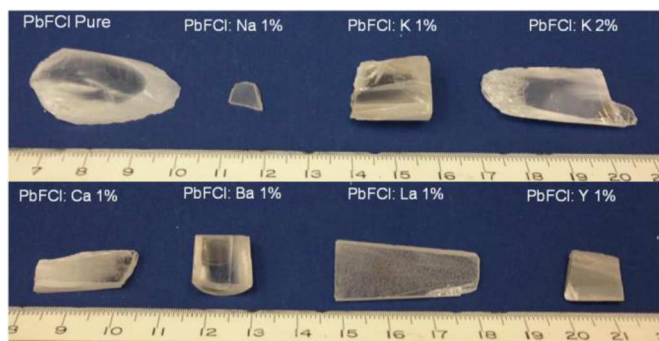


Fig. 3. Photographs of pure and doped PbFCl samples.

hole on the Tyvek paper. For the photo-luminescence (PL) spectra and photon excited decay kinetics measurements, an Edinburgh FLS920 spectrometer was used with the Xe lamp and nanosecond lamp as excitation sources. The scintillation light output (LO) was measured by using a Hamamatsu R2059 PMT with a bi-alkali photo-cathode and a quartz window. For the LO measurement, the samples were wrapped with PTFE Teflon film. A ^{22}Na source was used to excite the samples. The γ -ray peak positions were determined by a simple Gaussian fit with systematic uncertainty of 1%.

A. X-ray Excited Luminescence

Fig. 4 shows XEL of all samples measured at room temperature. Only one emission band peaked at 400 nm was observed in XEL spectrum of pure PbFCl samples, as shown in Fig. 4(a). No variations were found in Ca, Ba, La and Y doped samples as shown in Fig. 4(e), 4(f), 4(g), and 4(h). Three emission bands were found in a Na doped sample with peaks around 340, 390, and 500 nm, as shown in Fig. 4(b). The strongest emission band peaking at 500 nm was also observed by Zhang *et al.* in an Na doped PbFCl sample [8]. Broad emission spectra were also found in two K doped PbFCl samples, as shown in Fig. 4(c) and 4(d). They were decomposed to two emission bands peaks around 400 and 550 nm by Gaussian fit. It is interesting to note that both Na and K doped PbFCl samples show the secondary emission band at 500 nm. This may be due to the monovalent cation doping of Na and K ions. No secondary emission was observed in Ca, Ba, La, and Y doped samples.

B. Photo-Luminescence and Its Temperature Dependence

Fig. 5 shows a PL spectrum for a K doped sample measured at 77 K with excitation photon energy of 4.88 eV. The photo-luminescence is decomposed to three emission bands at 2.27, 2.85 and 3.39 eV by Gaussian fit. Considering the emission bands at 2.85 and 3.39 eV, the similar cation exciton emission peaking at 2.93 and 3.81 eV with the exciton excitation of 4.7 eV at 8 K in PbCl_2 was also reported [9]. It may be reasonable that the emission bands at 2.85 and 3.39 eV is due to the annihilation of the localized self-trapped exciton which associates with the Pb^{2+} ion close to the Schottky-like defects [9], [10].

Since the emission band around 2.27 eV is also observed in Na doped PbFCl [8], the emission band at 2.27 eV observed in the PbFCl:K sample is not specific to K^+ ions. It thus is

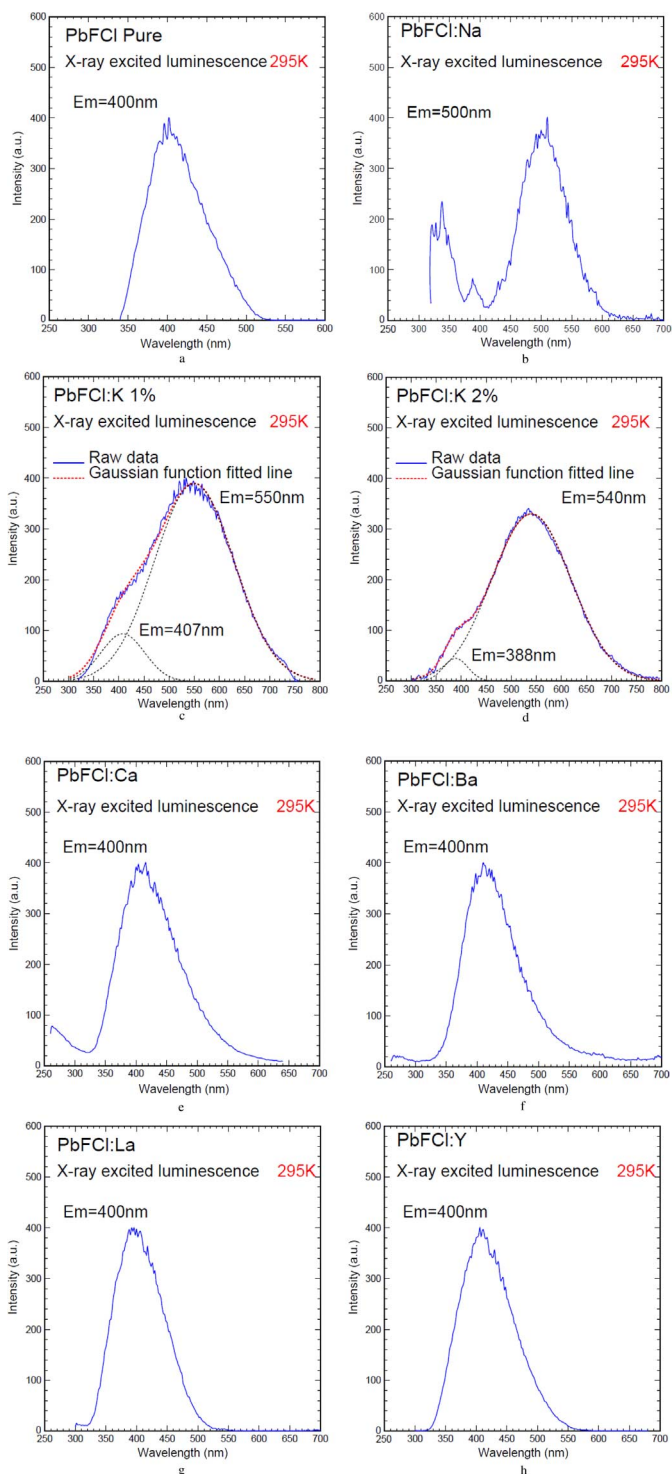


Fig. 4. X-ray excited luminescence spectra are shown for: a. Pure PbFCl; b. PbFCl:Na; c. PbFCl:K 1%; d. PbFCl:K 2%; e. PbFCl:Ca; f. PbFCl:Ba; g. PbFCl:La; and h. PbFCl:Y.

suspected that the luminescence center of the emission band peaked at 2.27 eV is self-trapped exciton with a configuration of $(\text{Pb}^{3+} + \text{electron})$ with the Pb^{3+} ions induced by the K^+ ions doping. An emission band peaked 2.5 eV was also observed in PbCl_2 at the temperature lower than 100 K, and was attributed to self-trapped exciton with the configuration of $(\text{Pb}^{3+} + \text{electron})$ [11]. Because of the K^+ ions doping, the configuration of $(\text{Pb}^{3+} + \text{K}^+)$ is more stable in PbFCl:K

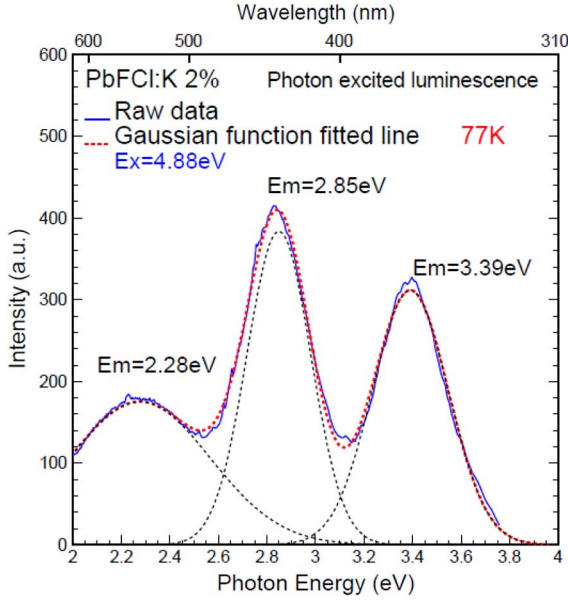


Fig. 5. PL spectrum measured at 77 K for a K doped sample.

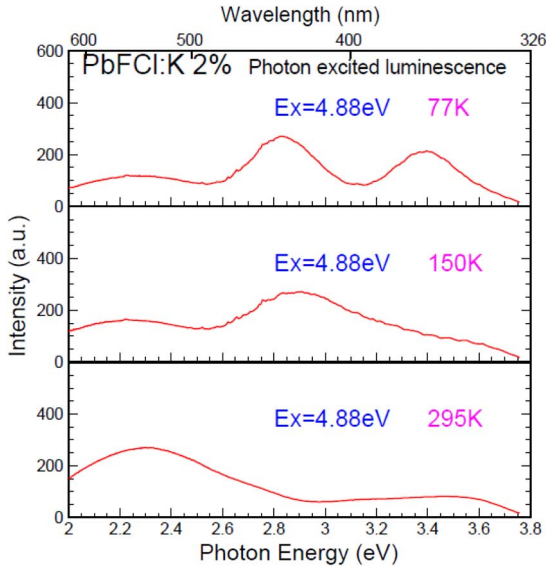


Fig. 6. PL spectra of a K doped sample measured at 77, 150 and 295 K.

than ($\text{Pb}^{3+} + \text{Pb}^+$) in PbCl_2 , leading to the emission band at 2.27 eV observed in PbFCl:K at the room temperature.

Fig. 6 shows a comparison of the PL spectra measured at 77, 150 and 295 K for a K doped PbFCl sample. The intensity of all three emission bands decreases when the temperature increases. The relative intensity of the emission band peaked at 2.27 eV, however, increases when the temperature increases.

Fig. 7 shows the normalized PL intensity of three emission bands as a function of temperature. The decrease of the intensity for all three emission bands is caused by a thermal quenching effect, similar to what is observed in XEL intensity for pure PbFCl crystals [12]. Since all three emission bands are due to forbidden transitions, the observed strong thermal quenching effect in PbFCl:K is consistent with the self-trapped exciton (STE) model [11].

Fig. 8 shows that the relative intensity of the 2.27 eV band increases while the other two bands decrease, indicating that the

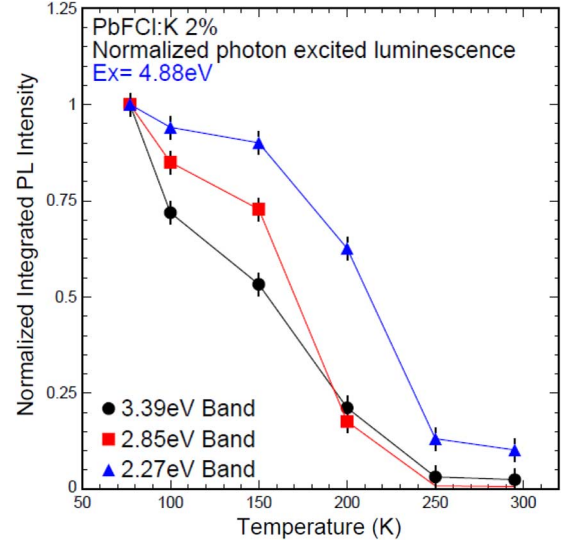


Fig. 7. Normalized PL intensity as a function of temperature.

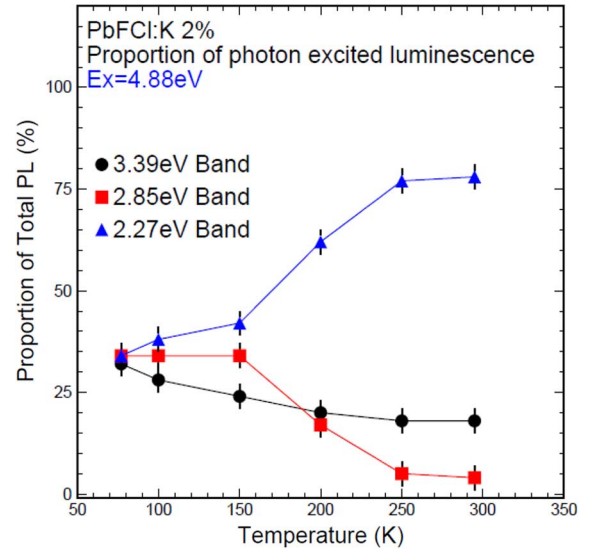


Fig. 8. PL intensity proportion of three emission bands as a function of temperature.

thermal quenching effect on the 2.27 eV band is weaker than the other two bands.

C. Decay Kinetics and Temperature Dependence

The decay kinetics of PbFCl:K 2% and its temperature dependence were measured by an Edinburgh FLS920 spectrometer with the width of the excited light pulse at a level of one nanosecond.

Fig. 9 shows the decay kinetics of three emission bands measured at 77 K for PbFCl:K 2% with the excitation photon energy of 4.88 eV. The decay time is obtained by using the following function:

$$S(t) = \int_0^t E(t')R(t-t')dt' \quad (1)$$

where $S(t)$ represents the measured fluorescence spectrum, $E(t)$ represents the instrumental response, and $R(t)$ represents

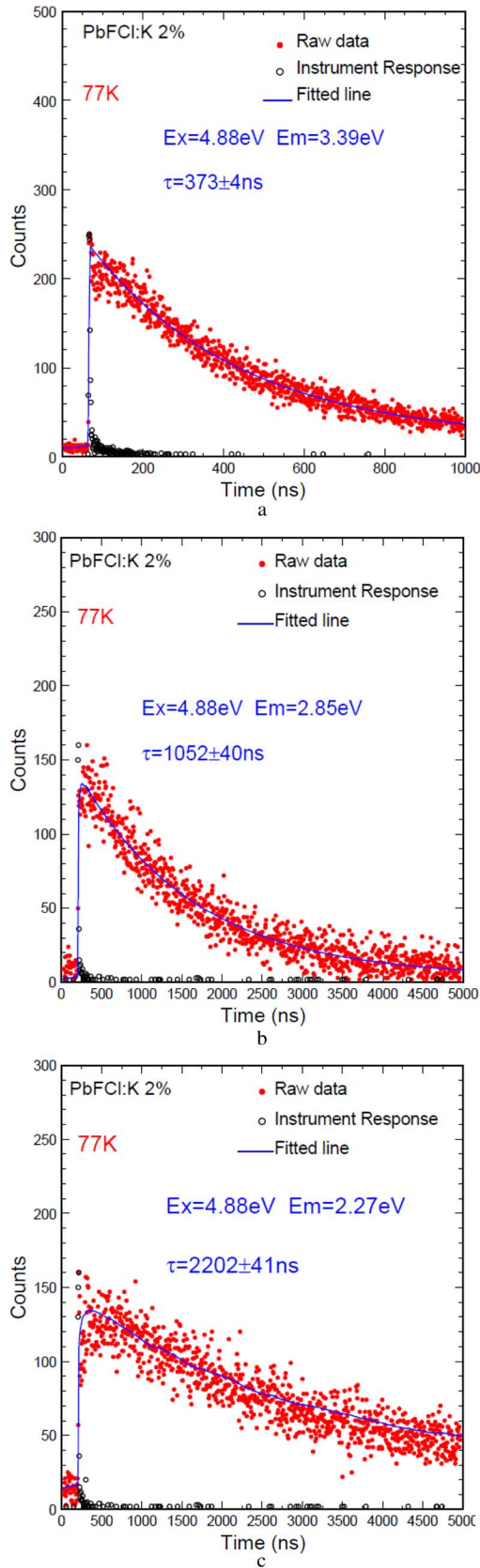


Fig. 9. Decay kinetics of three emission bands of PbFCl:K 2% measured at 77 K for three emission bands at (a) 3.39 eV, (b) 2.85 eV, and (c) 2.27 eV.

a theoretical decay model function. The decay time of emission bands at 3.39, 2.85 and 2.27 eV was determined to be 373,

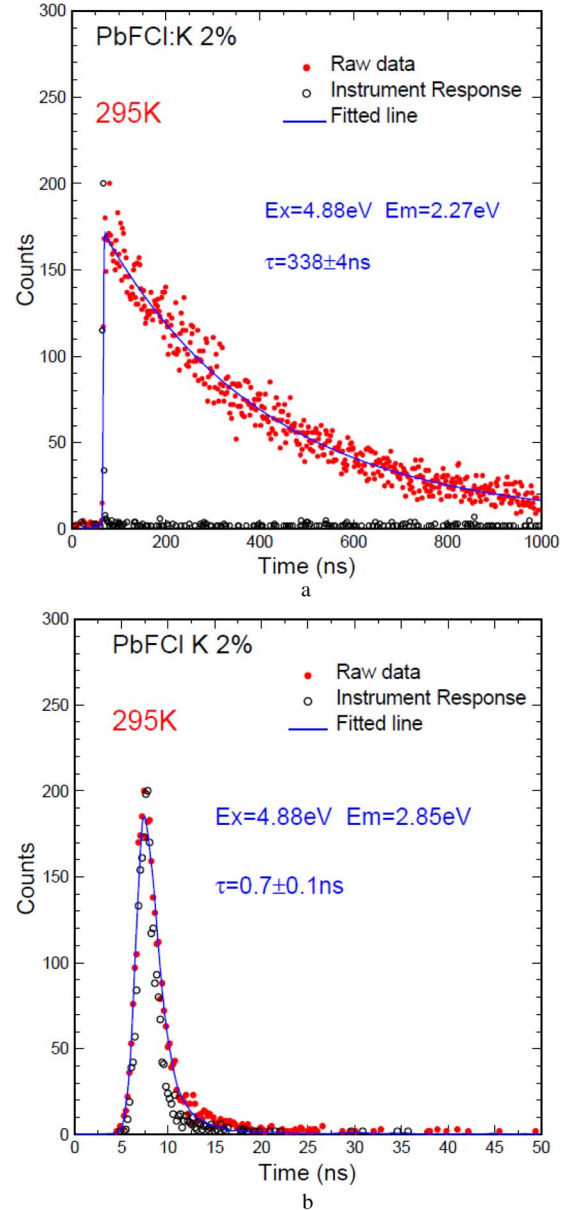


Fig. 10. Decay kinetics of two emission bands of PbFCl:K 2% measured at 295 K for emission band at (a) 2.85 eV and (b) 2.27 eV.

1052 and 2202 ns, respectively, at 77 K. The slow decay time at 77 K also indicates that the luminescence of sample PbFCl:K is due to STE related luminescence which was also observed in PbCl₂ [11].

Fig. 10 shows the decay kinetics of two emission bands measured at 295 K for PbFCl:K 2% with excitation photon energy of 4.88 eV. The decay time of the emission bands at 2.85 and 2.27 eV is found to be 0.7 and 338 ns, respectively, at 295 K. The decay kinetics of the emission band at 3.39 eV is too fast compared with time resolution of the instrument (0.5 ns), and so cannot be used for the decay time extraction.

Fig. 11 shows the decay time of three emission bands as a function of temperature for sample PbFCl:K 2% with the excitation photon energy of 4.88 eV. The decay time of all emission bands decreases when the temperature increases, caused also by the thermal quenching effect. Since the temperature variation

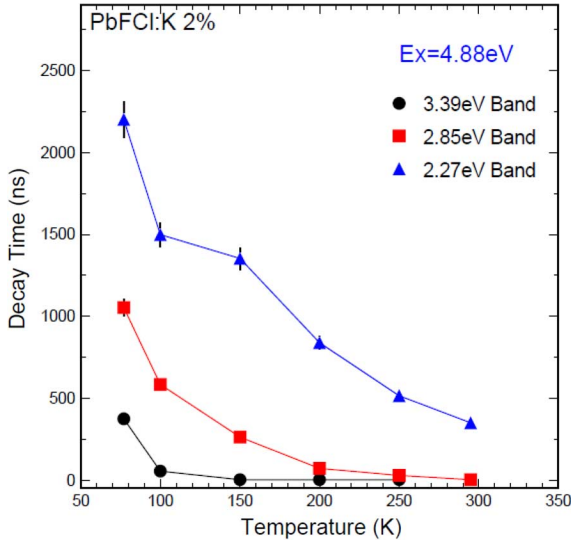


Fig. 11. Decay time as a function of temperature.

of the decay time for emission band at 3.39 eV was similar to that for the emission band at 2.85 eV, it is reasonable to assume that both emission bands are due to the annihilation of localized STE.

D. Radio-Luminescence Decay Kinetics and Light Output

Fig. 12 shows the light output as a function of the integration time and corresponding exponential fit for samples of (a) pure PbFCl, (b) PbFCl:K 1% and (c) PbFCl:K 2%. All samples were excited by a Na-22 gamma-ray source. The results of the decay time and LO for the fast and slow components are listed in Table I.

The decay time of pure PbFCl is 3.1 ns excited by gamma-rays and the corresponding light output is 11.6 p.e./MeV which is at the same level as PbWO₄ [13] but much lower than the LO (20% of BGO) of PbFCl sample reported by Chen *et al.* [14]. The PbFCl:K 1% and PbFCl:K 2% samples show two scintillation components. While the decay time and light output of the fast component are consistent with the pure PbFCl, the decay time of the slow component is consistent with the photo-luminescence emission band at 2.27 eV discussed above. It is also noticed that the light output of the slow component increases when the K concentration increases.

IV. SUMMARY

With density of 7.11 g/cm³, cutoff edge at 280 nm and intrinsic emission peak around 400 nm PbFCl crystals are a good candidate material for the HHCAL detector concept. Pure and doped PbFCl crystals can be grown with potentially low cost by the modified Bridgman method in air atmosphere. In order to grow the crystal of high quality, F/Cl ratio in raw materials needs to be optimized.

K ions doping in PbFCl introduces a slow luminescence center peaked at 550 nm. Its intensity increases when the K concentration increases. The thermal quenching effect on the 550 nm PL band is weaker than the other two PL bands. The decay time of the 550 nm emission band is about 2 200 ns at 77 K and 340 ns at 295 K. The emission bands at 2.85 and

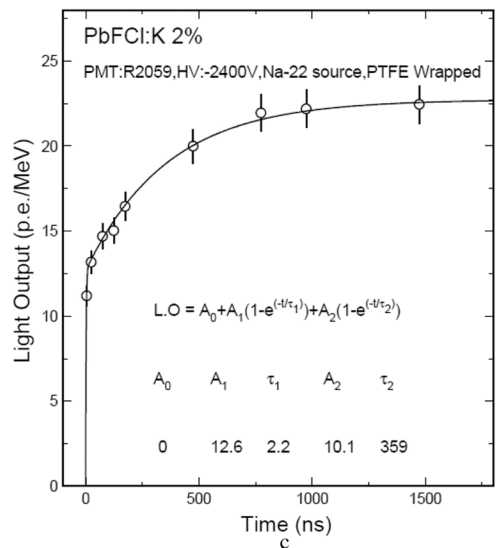
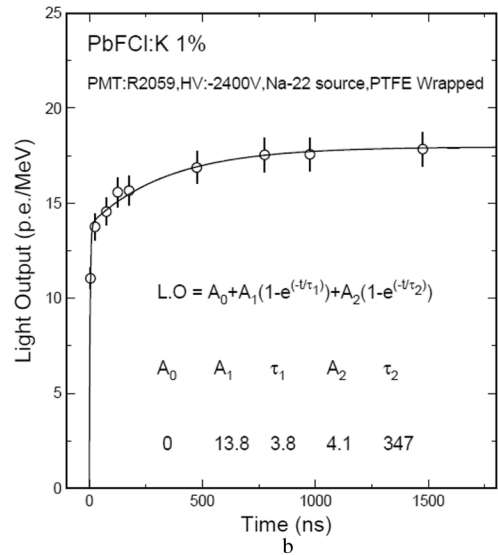
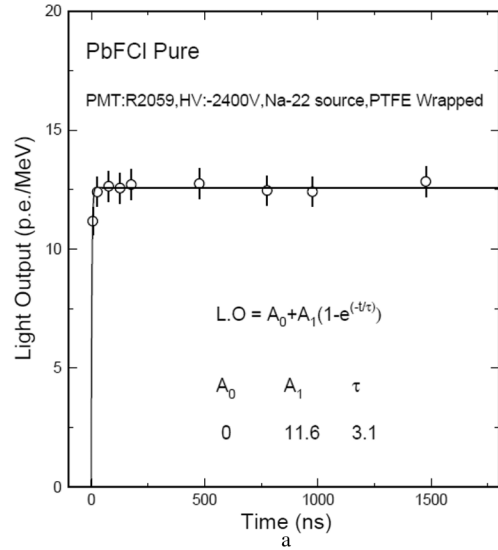


Fig. 12. Decay kinetics of radio-luminescence and light output are shown for: a. Pure PbFCl, b. PbFCl: K 1%, and c. PbFCl: K 2%.

3.39 eV may be due to the annihilation of the localized STE associated with the Pb²⁺ ion close to the Schottky-like defects.

TABLE I
SUMMARY OF LO AND DECAY TIME

	LO of Fast Component (p.e./MeV)	Decay time of Fast Component (ns)	LO of Slow Component (p.e./MeV)	Decay time of Slow Component (ns)
Pure PbFCl	11.6±0.8	3.1±0.8	-	-
PbFCl:K 1%	13.8±0.4	3.8±0.3	4.1±0.7	347±7
PbFCl:K 2%	12.6±0.4	2.2±0.8	10.1±0.8	359±14

The luminescence centers of emission band at 2.27 eV are STEs with a configuration of (Pb³⁺ + electron) induced by K⁺ doping.

This slow green scintillation light is useful for the discrimination between the scintillation light and the Cherenkov light for the HHCAL detector concept. A crucial issue for HHCAL is to grow PbFCl crystals of large size.

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