



## CsI(Na) micron-scale particles-based composite material for fast pulsed X-ray detection

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### ABSTRACT

We report a method for the preparation of fast scintillation composite material based on CsI(Na) micron-scale particles. The composite material was prepared by solidifying CsI(Na) micron-scale particles in an epoxy resin adhesive. The scintillation properties under X-ray excitation were investigated. The luminescence time characteristic of the CsI(Na) composite material is significantly improved, with the fall time range of 15.6–19.6 ns, over 20 times faster than that of bulk single crystal CsI(Na). Furthermore, the deliquescence property of CsI(Na) is overcome. The luminescence spectra show that the Na-related luminescence and self-trapped excitons luminescence of the composite material are strongly concentration-dependent. This kind of composite material could be a promising scintillator used in fast pulse X-ray detection.

### 1. Introduction

Sodium-doped cesium iodide (CsI(Na)) is an effective alkali metal halide inorganic scintillator. Due to the moderate density (4.53 g/cm<sup>3</sup>) and moderate atomic number ( $Z_{\text{eff}} = 54$ ), high light yield (38,500 ph./MeV), it has good stopping power and unique radiation response to heavily charged particles, gamma-rays and X-rays [1,2]. Bulks and thin films of CsI(Na) crystal have become an ideal scintillation detection material being applied to nuclear radiation detection, high-energy physics experiments, coherent neutrino–nucleus scattering detection, nuclear medical imaging and space exploration [3–6]. For example, the Weakly Interacting Massive Particle (WIMP) is a popular dark matter candidate in the universe. Dark matter may be observed by obtaining the nuclear recoil signals due to the elastic scattering between WIMPs and a target nuclei. CsI(Na) is a good candidate for dark matter direct detection because of its high neutron/ $\gamma$  discrimination ability [3,7]. However the scintillation decay time of bulk single crystal of CsI(Na) is as slow as 650 ns, which limits its application in fast pulse radiation field detection [8–10]. Additionally, the scintillation performance of CsI(Na) could be deteriorated when exposed to an air atmosphere, leading to a low detection efficiency in a high humidity condition [11]. Thus the CsI(Na) crystal needs to be encapsulated so that it can be isolated from the air atmosphere.

In the recent research, it is found that the scintillation decay time of CsI(Na) under X-ray excitation could be sped up from 650 ns to

19 ns when the size of CsI(Na) particles decreases to the micron-scale, providing a new approach to apply CsI(Na) to fast X-ray or gamma scintillator detection [12]. However, the micron-scale particles of CsI(Na) are hard to be directly applied to the radiation detectors due to the disadvantages of the hygroscopicity and difficulty in shaping. The epoxy resin adhesive has been widely used in the field of cementation due to the advantages of favorable mechanical properties, binding force, good transmittance and stability [13].

It could be a suitable method for curing CsI(Na) micron-scale particles to form a composite material with epoxy resin adhesive, which can not only retain the fast scintillation decay time characteristic but also overcome its disadvantages of deliquescence. The prepared micron-scale particles of CsI(Na) were isolated from the air atmosphere by means of being cured in epoxy resin adhesive. In the present work, a kind of scintillator composite material based on micron-scale particles of CsI(Na) and epoxy resin adhesive was successfully developed.

### 2. Experimental methods

#### 2.1. Preparation of CsI(Na) composite material

The bulk CsI(Na) single crystals were grown by the Bridgman–Stockbarger method, with 0.02 mol.% doping concentration of Na<sup>+</sup>.

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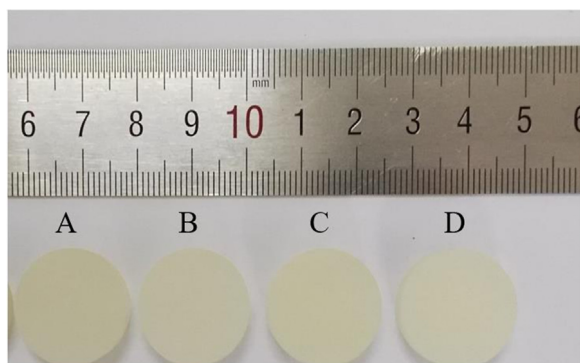


Fig. 1. Photographs of the samples.

The micron-scale particles of CsI(Na) were obtained by ball-mill treatment from a bulk CsI(Na) single crystal, and then the obtained particles were filtered by using a sieve with micron-scale holes in order to ensure the size ranging from 20–100  $\mu\text{m}$ . The CsI(Na) particles are dried in the electric oven for 60 min at the temperature of 105  $^{\circ}\text{C}$ . Finally, the particles are cooled for 20 min to minimize the impact of deliquescence.

The epoxy resin is fully mixed with ammonia curing agent in a beaker in a certain proportion. Stir the epoxy resin to fully react with the curing agent, and then add the filtered and dried CsI(Na) particles according to required mixture ratios. During the curing process, the CsI(Na) particles are continuously stirred to evenly suspend in the epoxy resin adhesive, forming a solid composite material. The composite material samples formed from epoxy resin adhesive solidification with 0.25, 1, 2.5 and 3.5 wt% (weight percentage) CsI(Na) particles are labeled as sample A, B, C, and D as shown in Fig. 1. The four samples have the same thickness of 8 mm and a diameter of 16 mm.

## 2.2. Scintillation properties measurements

### Measurement of time performance

The luminescence decay time of CsI(Na) composite material is studied by measuring the time response waveform of sample A, B, C, and D excited by a sub-nanosecond pulsed X-ray source. Fig. 2 is the schematic diagram of the time-response measurement setup. The average energy of the pulsed X-ray source is about 100 keV with a half-width pulse time of less than 0.8 ns. Two parts are included in the setup. One part is to detect the working state of the pulsed X-ray source, in which a plastic scintillator of ST401 facing the X-ray source

is closely coupled to a PMT (ETL 9850B, U.K.). The other part is used to measure the response waveform of the composite materials, in which the scintillation photons are collected by an ultrafast MCP-PMT after passing through a reflective path, consisting of concave mirrors and diaphragms in the dark chamber. The reflective optical path system is used to avoid interference from the X-ray source and increase the collection efficiency of scintillation photons. Finally, the output signals of the two PMTs are measured by oscilloscope (DPO7104).

### Measurement of luminescence spectra

We measured the emission spectra under the excitation of a portable X-ray source (12 W X-ray source manufactured by Moxtek Inc.). A spectrometer (Newport 74216) and a PMT (Newport 77360) were used to record the emission spectra of samples. The working voltage of the photomultiplier tube collecting fluorescence is  $-1000$  V. The voltage and current set by the X-ray source are 30 kV and 300  $\mu\text{A}$  respectively. The samples fixed at 5 mm away from the slit of the monochromator were excited by the X-ray source placed 14 cm away from the sample. The emission spectra were recorded for wavelength ranging from 250 to 700 nm which is determined by the response range of the photomultiplier tube.

## 3. Results and discussion

Fig. 3 shows the SEM image of the CsI(Na) particles, showing the particle size ranging from 20 to 100  $\mu\text{m}$ . The experimental transmission spectra of samples in the normal direction are shown in Fig. 4. The transmittance is low, with a minimum of 0.25% and a maximum of 2.5%. There are several reasons for the low transparency, including multiple internal reflection and scattering caused by the large size distribution of CsI(Na) particles and air bubbles mixed in the preparation of the samples. The larger the size distribution range is, the stronger the scattering will be, which will make the samples opaque. We will improve transparency by reducing air bubbles and reducing the size distribution of CsI(Na) particles in future sample preparation. Although the transmittance is not ideal, the material can be used to measure charged particles.

Fig. 5(a)–(d) show the time-response waveforms of sample A, B, C, and D. Due to the low vertical resolution of oscilloscope, we cannot fit the waveforms. So we use the 10%–90% rise-time and 90%–10% fall-time to characterize the time properties. The scintillation properties for the four samples are listed in Table 1. The sample A with the lowest concentration of CsI(Na) particles (0.25 wt%) has the fastest decay time (15.6 ns) and the slowest rise time (3.4 ns). As the concentration of CsI(Na) particles increases, the fall time increases to 19.6 ns and the rise time decreases to 2.8 ns for sample D with 3.5 wt%. These results are similar to the experimental results of Fang Liu et al. in

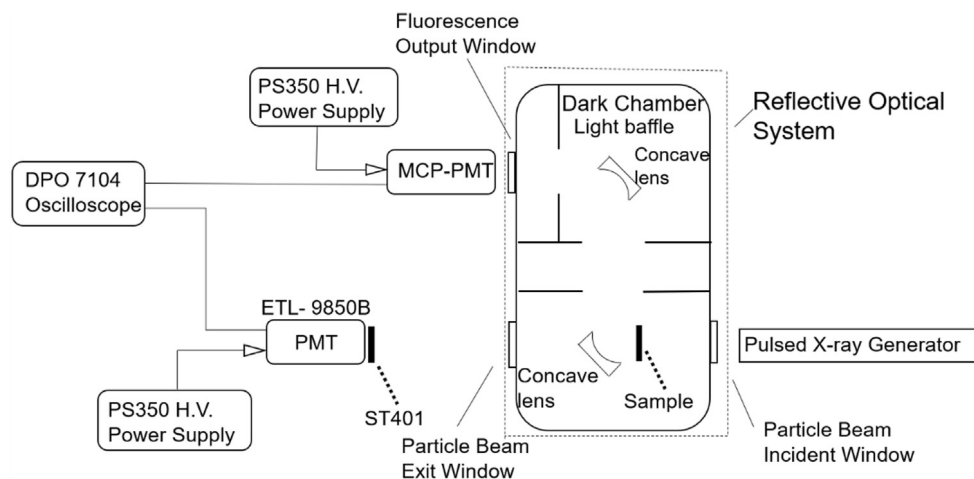


Fig. 2. Schematic diagram of time-response measurement experimental setup.

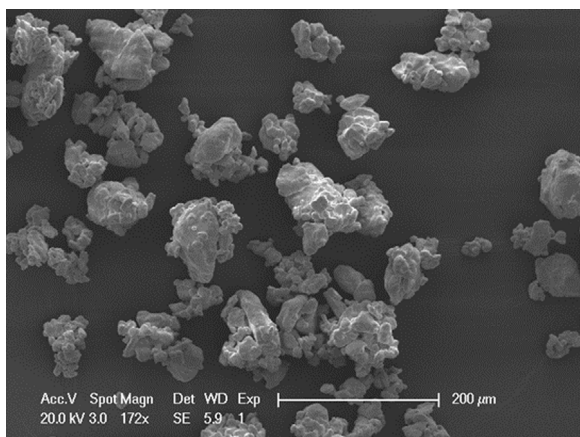


Fig. 3. SEM image of the CsI(Na) micron-scale particles.

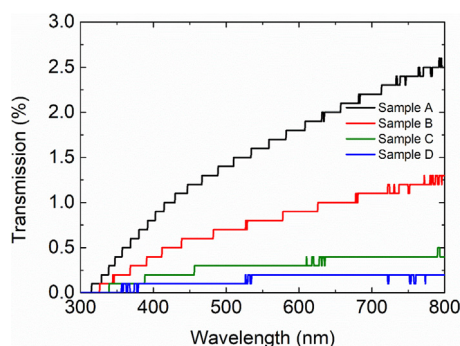


Fig. 4. Transmission spectra of the samples.

which the decay time of CsI(Na) micro particles with sizes between 20–864  $\mu\text{m}$  under pulsed X-ray excitation is about 19 ns [12]. The experimental results reported by Fang Liu et al. also showed that the decay time of bulk CsI(Na) crystal excited by pulsed X-ray is about 600 ns which is in agreement with the decay time of CsI(Na) crystal under gamma ray excitation reported by Sun et al. [3]. It verifies that the composite material maintains fast luminescence decay time characteristic of CsI(Na) micron-scale particles.

Fig. 6 shows the X-ray excited emission spectra of sample A, B, C, and D. The emission spectra of each sample have two main emission bands. The emission spectra peak at 316 nm and 405 nm for the sample A, 323 nm, 413 nm for the sample B, 335 nm, 443 nm for the sample C, 328 nm, 453 nm for the sample D. It is found that the peak position of 405 nm moves toward the long wavelength and the peak intensity of 405 nm increases significantly with raising the concentration of CsI(Na) particles. It is well known that the emission band peaking at 420 nm blue luminescence of CsI(Na) is attributed to electrons and holes recombination by a tunneling process associate with  $\text{Na}^+$  ions [14–16]. Ren et al. [8] shows that the emission wavelength of pure CsI is peaked at 318 nm which is close to 315 nm reported by Schotanus and 310 nm reported by Amsler and Woody [17–19]. The emission band peaking at 310 ~320 nm is attributed to self-trapped excitons from the host material CsI [20]. Na-related luminescence dominates in CsI(Na) crystal [21].

Table 1 shows the peak characteristics of the X-ray excited emission spectra of the CsI(Na) composite material. From Table 1, it is observed that with the increase of CsI(Na) concentration, the Na-related luminescence dominates. The peak area ratio (peak2 for Na-related luminescence / peak1 for self-trapped excitons luminescence) and peak intensity variation of samples exhibits the strong concentration dependence. For sample A with the lowest concentration of CsI(Na) particles,

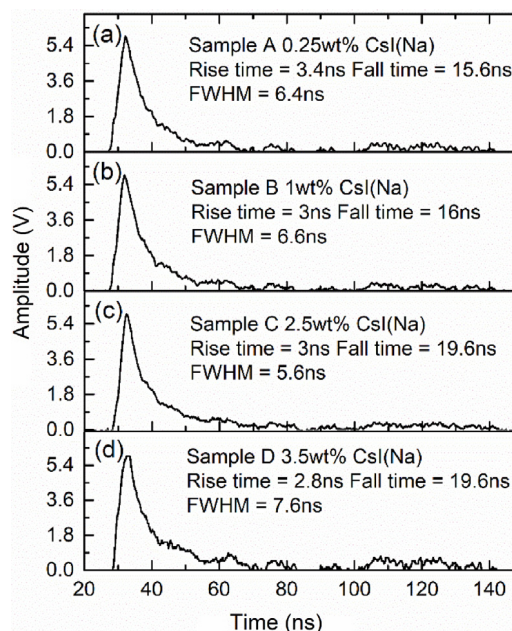


Fig. 5. Time-response of the samples excited by pulse X-ray.

Table 1

Peak characteristics of X-ray excited emission spectra of the CsI(Na) composite material.

Sample	Peak-I position (nm)	Peak-II position (nm)	Peak area ratio (peak2/peak1)
A	316	405	1.088
B	323	413	1.455
C	335	443	2.77
D	328	453	3.39

the area of peak 2 is approximately equal to that of peak 1. As the concentration of CsI(Na) particles increases, the area of peak 2 increases obviously. The peak area ratio and the intensity of peak 2 of sample D with the highest concentration is the maximum. For sample D, the area of peak 2 is four times that of peak 1. Scintillation time characteristics of the CsI(Na) composite material are listed in Table 2. From Table 2, each sample is characterized by the fast scintillation luminescence of CsI(Na) micron scale particles. According to Fang Liu et al. as the size of the CsI(Na) particles decreases, the surface increases and thus leads to an increase in surface defects. As a result, the increase in surface defects leads to a decrease in  $\text{Na}^+$  ions trapping excitons. Thus with the increase of surface defects, the surface quenching is amplified which speeds up the decay time of CsI(Na) particles. Although the surface effect of the defects can speed up decay time, it causes the reduction of luminous intensity. When the size of CsI(Na) particles is larger than 20  $\mu\text{m}$ , Na-related 420 nm luminescence dominates. However when the size of particles is reduced to the nanoscale, the self-trapped excitons luminescence of CsI dominates and Na-related luminescence becomes very weak, which is not conducive to X-ray detection. The luminescence of micron-scale particles is enhanced compared to the nanoscale particles with higher quantum efficiency. According to our experimental results, the luminescence of micron-scale particles is dominated by  $\text{Na}^+$  ions, which is consistent with results by Fang Liu [12]. Therefore choosing the suitable size is of great importance in the application of composite scintillation materials based on CsI(Na) particles.

#### 4. Conclusion

We have found a method to apply CsI(Na) micron-scale particles to act as scintillators in nuclear radiation detection. The disadvantages of

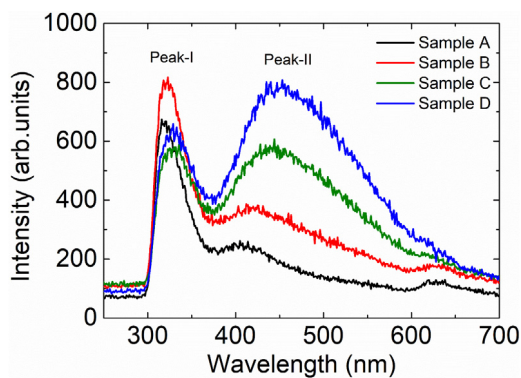


Fig. 6. X-ray excited emission spectra of the samples.

**Table 2**  
Scintillation time characteristics of the CsI(Na) composite material.

Sample	Concentration of CsI(Na) particles (wt%)	Rise time (ns)	Fall time (ns)	FWHM (ns)
A	0.25	3.4	15.6	6.4
B	1	3	16	6.6
C	2.5	3	19.6	5.6
D	3.5	2.8	19.6	7.6

CsI(Na) deliquesce and difficulty of shaping can be overcome by curing it in epoxy resin adhesive, obtaining a fast scintillation composite material in this way. We have investigated the time-response and emission spectra under X-ray excitation of the composite materials. Experimental results show that the material has a potential value for application in radiation detection and is possible to be used for fast pulse X-ray detection.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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