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Preparation and scintillation properties of translucent LiCaBO₃:Ce polycrystalline plates

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Abstract

Translucent LiCaBO₃:Ce thin plates were prepared by liquid phase sintering using LiBO₂ as a sintering aid, and their fluorescent and scintillation properties were investigated to examine the possibility to use as neutron scintillator. Since the initial part of the directionally solidified specimen contained a second phase of Ca₃B₂O₆, LiCaBO₃ may melt incongruently, and simple melt growth of LiCaBO₃:Ce is consequently difficult. Translucent thin plates 300 μm in thickness were successfully fabricated from LiCaBO₃:Ce sintered compacts. Although strong fluorescence with the peak wavelength of 390 nm was observed in photoluminescence measurement, scintillation light yield and detection efficiency by α-particle irradiation were rather poor. The diffuse reflectance spectrum of LiCaBO₃:Ce revealed existence of an absorption band other than Ce³⁺ bands in the ultraviolet region. The band may correspond to defect levels, which interrupt the energy transfer from the conduction band of the host to the 5d level of Ce³⁺ resulting in the degradation of the scintillation performance.

Keywords:

Neutron scintillator; Translucent polycrystalline thin plate; Liquid phase sintering; Grain growth; Borate

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1. Introduction

Neutron scintillators have been used for imaging and diffraction technologies and will find other application fields such as medicine and security systems with the progress of scintillation performance. ^3He gas have conventionally been used as a gas scintillator material due to its high neutron capture efficiency [1]; however, the ^3He resources are limited, and development of alternative materials has accordingly been required. A number of solid scintillators have so far been developed, for example, LiF/ZnS:Ag [2], Li-glass [3], and $\text{LiCaAlF}_6\text{:Ce}$ [4] etc. These solid materials have high densities in comparison with the gas type and highly efficient detection is expected. In neutron detection, a scintillation material is excited by the energy of the charged particles generated via the capture reactions between neutrons and nucleus of particular isotope species such as ^6Li or ^{10}B in the material. Consequently, the kind of the elements that form the host material is limited. In most solid neutron scintillators such as Li-glass and $\text{LiCaAlF}_6\text{:Ce}$ single crystals, only ^6Li is used as a neutron capturing isotope. Although the total energy of charged particle resulted from the reaction between neutron and ^{10}B is less than that from the neutron- ^6Li reaction, neutron capture cross-section of ^{10}B is much higher than that of ^6Li , and abundance ratio of ^{10}B is larger than ^6Li . Thus B-bearing materials have also been developed as neutron scintillators [5-7]; however, the light yield of such materials were relatively small.

LiCaBO₃:Ce was reported as a blue phosphor [8] based on the 5d→4f transition of Ce³⁺ substituted in the Ca²⁺ site; however, it has not been studied as a scintillation material. Since LiCaBO₃:Ce is composed of relatively light elements, low sensitivity to gamma-ray from the background under neutron measurement environment is expected. Furthermore, since Ce³⁺ usually exhibits intensive light emission and short decay time in conventional scintillator materials, LiCaBO₃:Ce is expected to exhibit excellent scintillation properties. According to the reported phase diagram of the pseudobinary system LiBO₂-CaO [9], LiCaBO₃ melts congruently at 915 °C indicating the possibility of melt growth such as Bridgman and Czochralski techniques. On the basis of these features, LiCaBO₃:Ce may be one of the candidates as a neutron scintillator material.

In this study, we attempted directional solidification of LiCaBO₃:Ce to investigate the possibility of its melt growth. Liquid phase sintering was also tried to obtain translucent thin plates of LiCaBO₃:Ce, and their fluorescence and scintillation properties were examined to discuss the possibility as a neutron scintillator.

2. Experimental

2.1. Solidification behavior of LiCaBO₃:Ce

Powders of LiBO₂(99 up %), CaCO₃(99.99 %) and CeO₂(99.9 %) were used as starting

materials. These raw materials were mixed with ethanol in agate mortar in the composition of $\text{LiCa}_{0.9925}\text{Ce}_{0.005}\text{BO}_3$. After forming under a uniaxial pressure of 100 MPa, the mixed powder was fired at 800 °C for 10 h in $\text{H}_2(4\%)/\text{Ar}$. The calcined compact was charged in a carbon crucible, which was then placed in a tube furnace with some tilting angle. After melting for 5 h, the melt was directionally solidified by reducing the temperature at a rate of 1.5 °C/h in N_2 atmosphere. This cooling rate corresponds to the linear growth rate of 0.5 mm/h on the basis of the temperature gradient of the tube furnace. The initial part of the obtained solidified specimen was ground and evaluated by X-ray diffraction (MiniFlex600, Rigaku).

2.2. Preparation of translucent $\text{LiCaBO}_3:\text{Ce}$ polycrystalline plates

The calcined powder of $\text{LiCa}_{0.9925}\text{Ce}_{0.005}\text{BO}_3$ prepared with the same process described above was mixed with LiBO_2 as a sintering aid. After forming pellets under a uniaxial pressure of 100 MPa, they were sintered at 800 or 820 °C for 50 or 100 h in $\text{H}_2(4\%)/\text{Ar}$, which was effective to reduce the tetravalent cerium to trivalent one. The obtained pellets were gray and its absorption could inhibit emission. Post-sintering annealing at 800 °C for 10 h in N_2 resulted in colorless pellets. The sintered compacts were polished to be mirror finish, followed by etching in hot water. The crystalline phases of the sintered compacts were identified by X-ray diffraction and their microstructures were observed with a scanning electron microscope (JSM-6390LVS, JEOL). The polished surfaces of the sintered compacts

were adhered to glass plates with epoxy resin. The compacts were then ground to be 300 μm in thickness resulting in translucent thin plates.

2.3. Optical characterization of $\text{LiCaBO}_3\text{:Ce}$

As a method to easily check the light emission by photons, the sintered bodies were irradiated with handy UV lamp (AS ONE, Japan) having a wavelength of 365 nm. After that, fluorescence properties were investigated. The measurements of photoluminescence spectra were carried out using a JASCO FP-6500 (JASCO.CORDERATION, Japan)

The scintillation properties for α -particles were evaluated using ^{241}Am . The energy of α -particles emitted from ^{241}Am approximately corresponds to the energy of the charged particles generated by the capture reactions between a neutron and a nucleus of ^6Li . Accordingly, if scintillation for α -particles was observed, scintillation for neutrons is surely expected. A thin copper plate with a hole of 2 mm in diameter was placed between the α -particle source and the sample to regulate the flux of α -particles. The specimen was fixed on the photomultiplier tube with the aid of optical grease. A photomultiplier tube (H7195, Hamamatsu Photonics), a delay line amplifier (460, Ortec), a pulse stretcher (542, Ortec), and a multi-channel analyzer (WE7562, Yokogawa Electric) were used to evaluate the response for α -particles. The integration time constant of the delay line amplifier was set at 250 ns, considering the decay time of the scintillators.

3. Results and discussion

3.1. Solidification behavior of LiCaBO₃:Ce

Fig. 1(a) shows a directionally solidified ingot of LiCaBO₃:Ce. Since the initial part of the ingot is rounded due to the poor wettability of the melt to the carbon crucible, the definitive point from which solidification started is unclear. A large portion that is thought to surely contain the start point is therefore examined by the X-ray powder diffraction. As shown in Fig. 1(b), the major phase in the portion is LiCaBO₃:Ce but formation of an appreciable amount of Ca₃B₂O₆ can be observed. This result indicates that LiCaBO₃ may melt incongruently and Ca₃B₂O₆ is the initial phase for the melt composition of LiCaBO₃. In the reported phase diagram for the pseudobinary system of LiBO₂-CaO [9], the difference in the melting temperature of LiCaBO₃ and eutectic temperature for the LiCaBO₂-CaO system is very small and the eutectic composition is very close to the LiCaBO₃ composition. Since the amount of Ca₃B₂O₆ was small, peritectic and liquidus temperatures could be confused as eutectic and melting temperatures, respectively. Even though LiCaBO₃ melts incongruently, the single crystal of LiCaBO₃ can be grown by using an appropriate flux. In fact, relatively large LiCaBO₃ grains were obtained in the ingot; however, the crystal quality was rather poor due to the existence of numerous bubbles. The bubbles are thought to be formed by

constitutional super-cooling because of the high viscosity of the borate-based melt. The purpose of the present study is to examine the possibility of $\text{LiCaBO}_3:\text{Ce}$ as a neutron scintillator and this could be done transparent or translucent specimen can be obtained. Therefore we focused to prepare sintered compact of $\text{LiCaBO}_3:\text{Ce}$ with large grains instead of single crystal growth, which is a challenging task.

3.2. Characterization of the polycrystalline thin plates

Fig. 2 shows microstructures of the sintered compacts. All the samples comprised only the LiCaBO_3 phase and no secondary phase was observed. In both samples (a) and (b) sintered at 800 °C, the grains that had particle size 20 to 50 μm were observed. The uniformity of the compact (b) sintered for 100 h was improved better than that of (a) sintered for 50 h. For the sintering time of 50 h, larger size of grains were observed in the sample sintered at 820 °C than that sintered at 800 °C. The relative densities of all samples were about 90 %. Since the pores in the compacts scatter light and deteriorate transmittance, it is desirable to eliminate as much as possible. All the samples contained a number of pores as shown in Fig. 2, and they were consequently opaque; however, the grain size of 50 μm may be sufficient to obtain translucent thin plates by grinding them to the thickness of a few hundreds of micrometers.

When a sintered compact was excited by a UV lamp, it emitted strong blue light as shown

in Fig. 3(a). Fig. 3(b) presents the photoluminescence spectra of LiCaBO₃:Ce in UV-visible range. Intensive blue fluorescence peaked at 390 nm and 420 nm corresponding to the 5d→4f transition of Ce³⁺ was observed with the excitation wavelength of 360 nm similar to that reported in [8]. The both excitation and fluorescence spectra are composed of double bands because the 4f level of Ce³⁺ splits in two levels of ²F_{2/7} ²F_{2/5} due to the spin-orbit interaction.

Polycrystalline LiCaBO₃:Ce thin plates were fabricated by grinding the sintered compact to the thickness of 300 μm. The thin plates were translucent as shown in Fig. 4. Since the total energy of charged particles resulted from the nuclear reaction between neutrons and nuclei of ⁶Li and ¹⁰B approximately corresponds to that of an α-particle emitted from ²⁴¹Am radiation source (5.5 MeV), simple measurements under α-ray irradiation were performed as a preliminary experiment instead of neutron irradiation. As-shown in Fig. 5, a broad energy band centered at 240 channel was obtained in the measurement for 5 minutes and this signal was confirmed not to be background or noise on the basis of blank test. From this result, we revealed for the first time that LiCaBO₃:Ce can emit scintillation light under the irradiation of α-particles. However, the light yield was about one thirty of that of Li-glass and the counts was also much smaller than expected for the measurement time of 5 minutes even though intensive fluorescence was observed under UV-light irradiation.

The low light yield and small counts are attributable to defect levels. Fig. 6 shows the diffuse reflectance spectra of LiCaBO₃:Ce and undoped one. For the Ce-doped sample, a

broad absorption band was observed in a shorter wavelength region than the absorption bands of Ce^{3+} around 340 nm and 370 nm due to $5d \leftarrow 4f$ transition. This absorption is attributable to defect levels formed by substituting aliovalent Ce^{3+} in Ca^{2+} site. A certain type of point defect should be introduced in the host lattice in order to accommodate Ce^{3+} in Ca^{2+} site and to keep electroneutrality. Although detailed investigation is necessary to clarify the type of the defect, excess oxide ion or cation deficiency are possible as the defect and in this case the latter is probable since oxygen is covalently bonded to boron to form BO_3^{3-} anion in the host crystal structure. The resulting cation deficiency possibly forms defect level below the conduction band. In the case of α -particle irradiation, the excited electrons from the valence band of the host crystal may be trapped at these defect levels and energy transfer to Ce^{3+} ions is consequently suppressed. In contrast, intensive blue fluorescence is observed in the case of photoluminescence because Ce^{3+} is directly excited. In scintillation mechanism, the excitation and recombination process of the host crystal is indispensable in order to transfer the energy to active ions, and the existence of such defect levels between the conduction band of the host crystal and excitation level of the active ions are responsible to the deteriorated scintillation performance.

4. Conclusions

LiCaBO₃ may melt incongruently and is difficult to be grown by a simple melt growth technique. As an alternative to a single crystal, translucent polycrystalline thin plates 300 μm in thickness were successfully prepared from sintered compacts of LiCaBO₃:Ce comprising grains of about 50 μm, and their scintillation properties were investigated. Although the scintillation light was observed from LiCaBO₃:Ce under the irradiation of α-particles for the first time, the light yield was not so large as compared with the result of photoluminescence and counts were also much smaller than expected for the measurement time. The diffuse reflectance spectrum of LiCaBO₃:Ce revealed defect levels under the conduction band of the host crystal and these levels may appreciably limit the energy transfer from host to Ce³⁺ resulting in rather poor scintillation performance.

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Figure captions

Fig. 1. (a) The solidified specimen, (b) XRD pattern of the initial part of the solidified specimen. The part surrounded by a yellow circle corresponds to its part.

Fig. 2. Microstructures of the $\text{LiCaBO}_3\text{:Ce}$ sintered compacts: (a) Sintered at 800 °C for 50 h; (b) Sintered at 820 °C for 50 h; (c) Sintered at 800 °C for 100 h.

Fig. 3. (a) Luminescence of sample when irradiated with UV handy lamp (ex.: 365 nm). (b) Fluorescence/excitation spectra of the $\text{LiCaBO}_3\text{:Ce}$ sintered compact.

Fig. 4. A translucent $\text{LiCaBO}_3\text{:Ce}$ polycrystalline thin plate. The thickness is 300 μm .

Fig. 5. Pulse height spectrum of the $\text{LiCaBO}_3\text{:Ce}$ sintered specimen for 5.5 MeV α -particle irradiation. Measurement time is 5 min.

Fig. 6. Diffuse reflectance spectrum of $\text{LiCaBO}_3\text{:Ce}$ powder. Red line is for the Ce-doped sample and black one is for the undoped sample.

Fig. 1

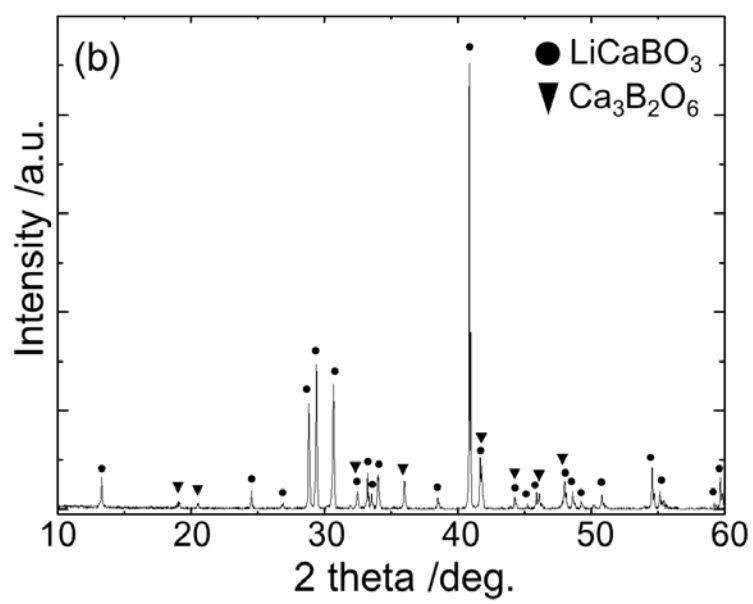
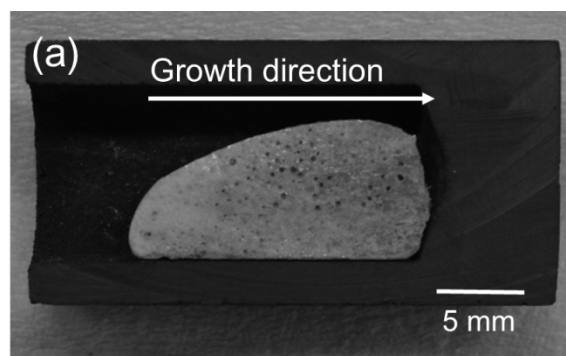


Fig. 2

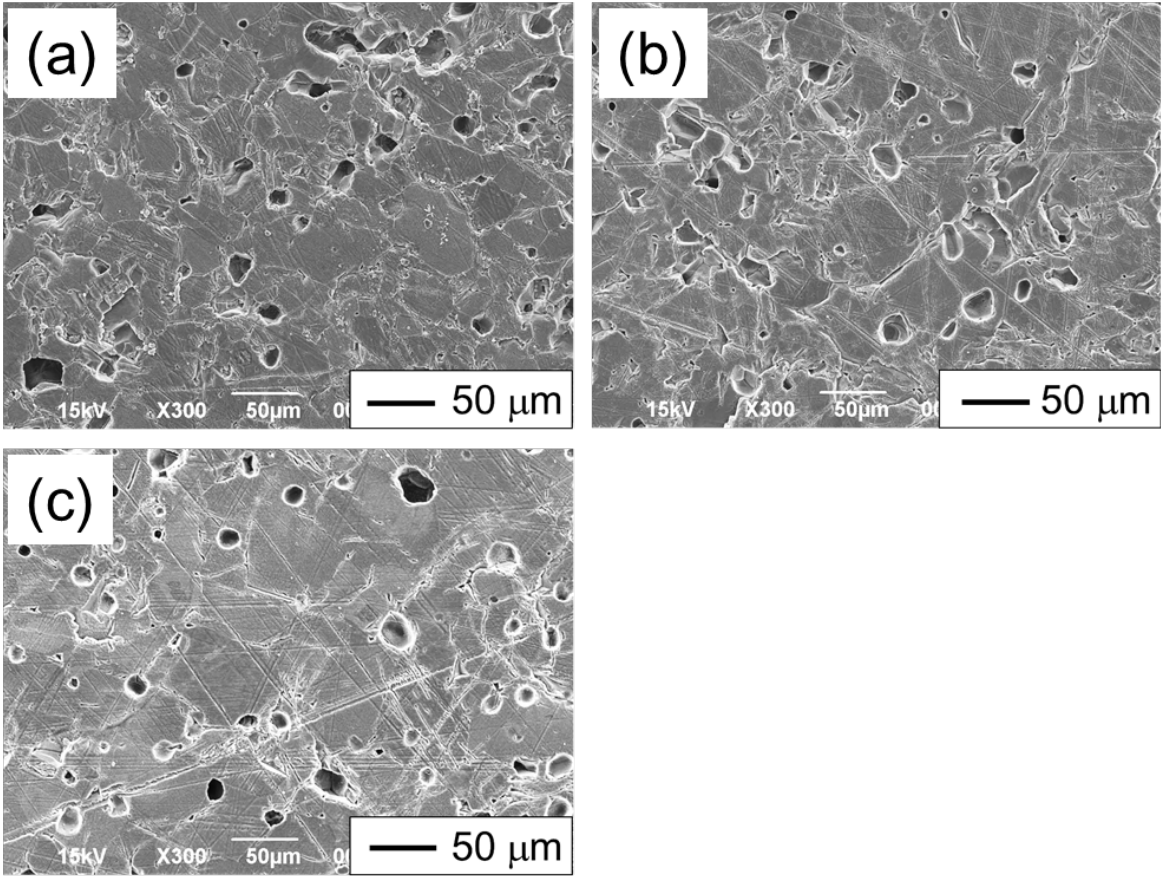


Fig. 3

(a)



(b)

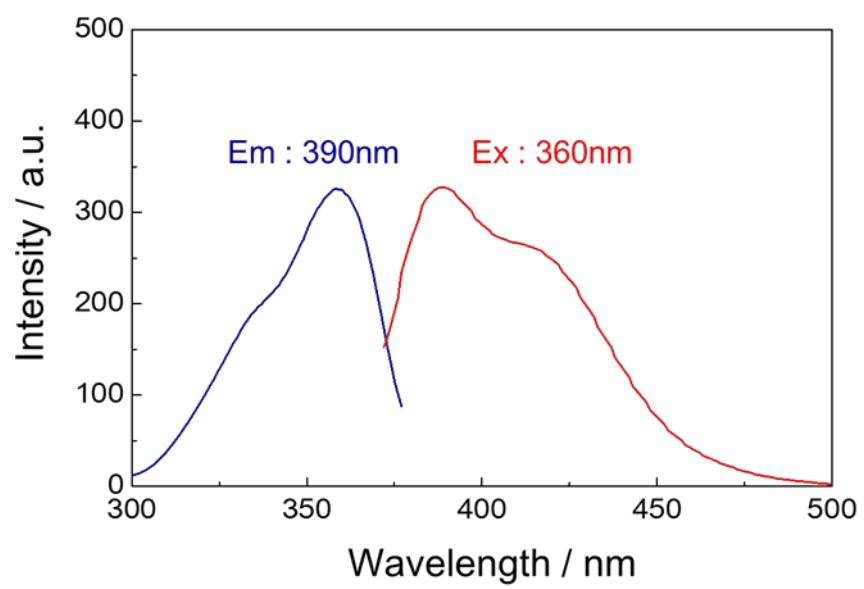


Fig. 4

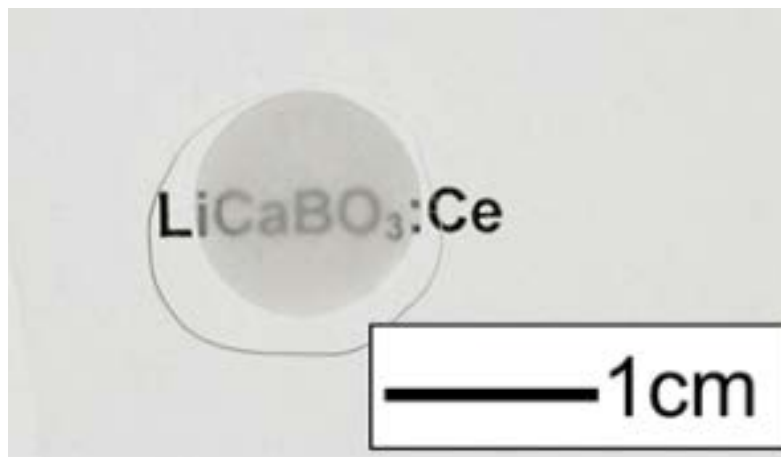


Fig. 5

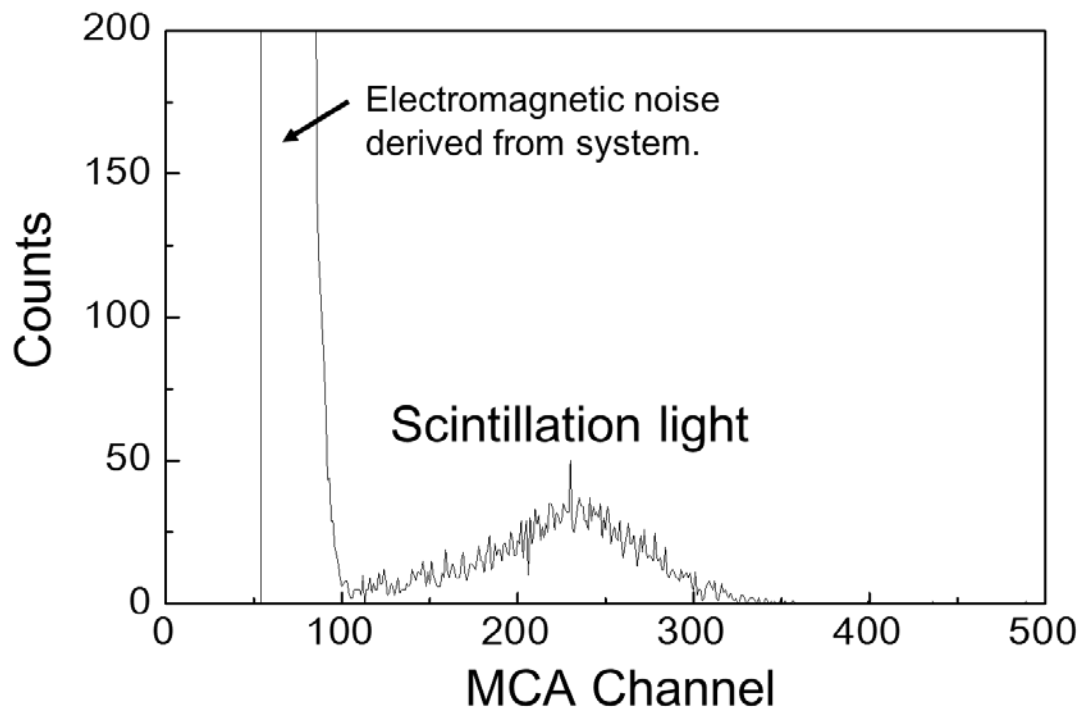


Fig. 6

