開発研究：新硼酸スキュリッターサーの開発研究

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Inorganic scintillator materials are employed in today's radiation detectors for medical diagnostics, industrial inspection, dosimeter, nuclear medicine, and high-energy physics using X-rays, gamma-ray, neutron, and so on. Especially the scintillator materials are much interesting for the application as thermal neutron detectors. The need for thermal neutron detectors is rapidly expanding with the increasing use of spallation neutrons as in the accelerator of the Spallation Neutron Source (Oak Ridge, USA) and the Japanese Neutron Spallation Source (Tokai, Japan).

Most common thermal neutron detector with high stopping power is $^3$He gas counter. However, unfortunately, $^3$He gas supply crisis is strictly limited in recent years. By these reasons, alternative detector such as a transparency bulk crystalline scintillator coupled with a photo-detector is strongly required. The neutron detection efficiency depends mainly on elements in scintillator materials. $^6$Li and $^{10}$B have high cross section ($^6$Li: 940 barn and $^{10}$B: 3836 barn) to thermal neutrons and convert them into ionizing particles according to the $^6$Li(n, αt) and $^{10}$B(n, α)$^7$Li reaction. After the reaction, charged particles ionize and excite scintillator, and then scintillation light is produced along their ionization tracks. Scintillator material must be constituted from light elements for low γ-rays background sensitivity. In addition, ideal scintillator should have a high light yield, and be transparent and easy to produce.

This thesis provides developments of new borate based crystalline scintillators for thermal neutron detection. Generally, there are many required parameters for neutron scintillators, application by application. Here, we pay attention to particularly four kinds of parameter for the development of neutron scintillator materials below.

(1) To obtaining high detection efficiency of neutron signal, scintillator material must be included large number of isotope which has large neutron captures cross section such as $^6$Li and $^{10}$B.

(2) To discriminating signals between γ-ray and neutron, scintillator material must have low sensitivity to γ-ray backgrounds.

(3) To obtaining the high detection efficiency and the possibility of n/γ discrimination, scintillator material need high absolute
light yield for neutron.

(4) From a practical application standpoint for neutron detectors, scintillator material must have no hygroscopicity and cleavage crack.

By the reasons, in this study, we choose YCa$_4$O(BO$_3$)$_3$, SrB$_2$O$_4$, CaB$_2$O$_4$, and Ca$_3$(BO$_3$)$_2$ single crystals as host material, and experiment with crystal growth and evaluation of scintillation characterization. Thus, we will develop scintillation material for alternative neutron detector.

Yttrium calcium oxyborate YCa$_4$O(BO$_3$)$_3$ is a useful nonlinear optical material with low symmetry (C m space group). It has a monoclinic crystal structure with the lattice parameter values of $a = 8.078$ Å, $b = 16.022$ Å, $c = 3.534$ Å, and $\beta = 101.19^\circ$. Some type of YCa$_4$O(BO$_3$)$_3$ crystalline scintillators activated with Ce$^{3+}$, Pr$^{3+}$, Eu$^{3+}$, Pb$^{2+}$, and Bi$^{3+}$ ions were grown by micro-pulling down (μ-PD) method. All samples were determined single phase with powder XRD patterns. The crystalline quality was found to be about 100 arcsec with FWHM of XRC analysis. In the photoluminescence spectra, strong emission peak around 400 nm due to 5d-4f transition of Ce$^{3+}$ was observed for Ce-doped crystal, while those of Pr$^{3+}$ 5d-4f transition $\lambda_{em} = \sim 300$ nm, Eu$^{3+}$ 4f-4f transition $\lambda_{em} = \sim 600$ nm, $^4$S$_0$$^2$P$_1$ transition of Pb$^{2+}$ $\lambda_{em} = \sim 360$ nm) and $^4$S$_0$$^2$P$_1$ transition of Bi$^{3+}$ $\lambda_{em} = \sim 380$ nm) were also identified for the crystals, respectively. By the $^{241}$Am ß-ray and $^{252}$Cf neutron irradiated pulse height spectra, the scintillators are not enough to satisfy scintillation light yield as neutron detector. For understanding the cause, we rechecked the scintillation process of Ce-doped crystal. First, we paid attention to the mysterious emission at 580 nm in 1.0 % Ce-doped crystal, and measured the excitation spectrum and decay time. In the excitation spectrum monitored at 580 nm, the peak was observed at 400 nm. Thus, there is overlap between the Ce$^{3+}$ 5d-4f luminescence peak (400 nm) and the excitation peak monitored at 580 nm.

This may means that the energy migration from excited 5d state of Ce$^{3+}$ to the emission process at 580 nm is caused. The decay time was calculated to be about 28 ns. This looks similar value of common Ce$^{3+}$ 5d-4f transition in oxide crystals. Therefore we gather that the emission at 580 nm is due to the transition of 5d-4f of Ce$^{3+}$ in other site because it is possible that Ce$^{3+}$ ions occupy both an Y$^{2+}$ site and two kinds of Ca$^{2+}$ sites. Besides, we concluded that the reducing of scintillation light yield was caused by the energy transition from Ce$^{3+}$ 5d excited state (400 nm) to that of other site (580 nm). Thus, in the case of YCa$_4$O(BO$_3$)$_3$ crystalline scintillators, it seems that it's difficult to obtain high scintillation efficiency using luminescence centers because of multi-lattice site in such Y$^{2+}$ and two kinds of Ca$^{2+}$ sites in the crystal.

SrB$_2$O$_4$ and CaB$_2$O$_4$ crystalline scintillators were explored because unlike the YCa$_4$O(BO$_3$)$_3$ crystals, they have no multi-lattice site. Both strontium metaborate SrB$_2$O$_4$ and calcium metaborate CaB$_2$O$_4$ crystals are belong to the orthorhombic system with space group Pbcm, and the lattice parameters are as follows: $a = 6.586$ Å, $b = 12.013$ Å, $c = 4.339$ Å and $Z = 4$ for SrB$_2$O$_4$, while $a = 6.216$ Å, $b = 11.607$ Å, $c = 4.283$ Å and $Z = 4$ for CaB$_2$O$_4$, respectively. Grown undoped and Ce-doped crystals showed no impurity and secondary phase by XRD patterns, however large cleavage behavior which is corresponding to the chains with slightly puckered infinite (B$_2$O$_4$)$_{2n}$ layers extending parallel to a c axis was observed. The lattice constants for $a$, $b$, $c$ became

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systematically change with Ce concentration. The calculated FWHM values of XRC were 180 arcsec for SrB$_2$O$_4$ and 110 arcsec for that of CaB$_2$O$_4$, respectively. Ce$^{3+}$ 5d-4f intense luminescence was observed for both Ce-doped crystals as well as that of photoexcitation one. Meanwhile undoped crystals showed broad intrinsic luminescence peak at 300-400 nm corresponding to the recombination of STEs in host lattice. Moreover we can also observe weak emission band around 300 nm for both Ce-doped crystals. These emissions attributed to a remnant of STEs emission absorbed by the 4f-5d transition of Ce$^{3+}$ ion. The calculated decay times were 190 ns, 2700 ns for undoped SrB$_2$O$_4$, 50 ns, 1430 ns for Ce-doped SrB$_2$O$_4$, 180 ns, 3600 ns for CaB$_2$O$_4$, and then 57 ns, 1580 ns for Ce-doped CaB$_2$O$_4$. It would resulted that one was fast component ascribed to 5d-4f transition of Ce$^{3+}$, then other was slow one due to the complex of STEs luminescence and delayed 5d-4f transition by energy migration from STEs to 5d excited state of Ce$^{3+}$. In the meteorite family, especially undoped and 0.5% Ce-doped CaB$_2$O$_4$ indicated high efficiency light yield, it was calculated to be about 3200 (CaB$_2$O$_4$) and 2200 (Ce-CaB$_2$O$_4$) photons per neutron.

Crystalline scintillators of Ca$_x$(BO$_3$)$_2$ activated with Ce$^{3+}$ were discussed for more improvement of host material because the cleavage cracks are serious problem from the viewpoint of practical application. Calcium orthoborate Ca$_x$(BO$_3$)$_2$ belongs to the trigonal structure with R$_3c$ space group, and the lattice parameters are as follows: $a = b = 8.6377$ Å, $c = 11.849$ Å, and $Z = 6$. As grown the undoped and Ce-doped crystals have high transparency and no cleavage cracks. By the XRD patterns, the CeO$_2$ phase was observed as a secondary phase when it becomes more than 1.0% nominal concentration of Ce. The lattice constants decreased once in 0.1% Ce-doped crystal and after that, it increased exponentially with increasing of Ce concentration. The decreasing is corresponding to the defect of cation ions such as Ca$^{2+}$ and B$^{3+}$ for the charge compensation. The FWHM value of 0.5% Ce-doped crystal was about 105 arcsec by XRC measurement. In the excitation spectra, two bands were observed at 280 and 350 nm, which were caused by the transitions between the level of excited 5d state and the ground 4f state of Ce$^{3+}$. It ascribe two excitation peaks to the 5d$_3$ levels at lower energy and the 5d$_4$ levels at higher energy of Ce$^{3+}$ due to the octahedral crystal field splitting. Strong emission peak around 400 nm originated from 5d-4f transition of Ce$^{3+}$ excited at both 275 and 345 nm. The emission intensity depends on the concentration of Ce$^{3+}$ ion, and it increases with increasing of Ce concentration. The values of photoluminescence decay component were found to be approximately 37-38 ns for all Ce-doped crystals regardless of the Ce concentration. Ce$^{3+}$ 5d-4f luminescence of 0.1% and 0.5% Ce-doped crystals also showed peaking around 400 nm under X-ray excitation. The position of the peaks was identical to that observed in the photoluminescence spectra. In addition, weak emission peak was observed around 310 nm for Ce-doped crystals. The emission peak is similar to that of Ce-doped CaB$_2$O$_4$, thus it is also believed to be attributed to a remnant of STEs emission absorbed by the 4f-5d transition of Ce$^{3+}$ ion. The scintillation decay components of 0.1% and 0.5% Ce-doped crystals were found to be about 340 and 260 ns, respectively. From these results, it was concluded that the decay component becomes faster when Ce concentration in the Ca$_x$(BO$_3$)$_2$ matrix increases. In the pulse height spectra under $^{252}$Cf irradiation, the absolute light yield of 0.5% Ce-doped crystal was determined to be about 2200 photons per neutron. At the same time, we also examined the crystal growth and evaluation of Pr$^{3+}$, Tm$^{3+}$, Eu$^{2+}$, $^{3+}$,
Cu⁺-doped Cas(BO₃)₂. The crystals were grown with μ-PD method. After polishing, we measured optical and scintillation characterization of all sample as well as Ce-doped crystals. As a result of measurements, the crystals showed α-ray response such as radioluminescence, scintillation decay and pulse height spectra, though their light yield were insufficient under irradiated by ²⁵²Cf neutron. Thus we concluded that Ce-doped Cas(BO₃)₂ crystals are practical scintillator material as neutron detector which indicate high light yield, non cleavage crack and hygroscopic.

Ce-doped Cas(BO₃)₂ crystalline scintillator was grown using conventional CZ technique for combining a 64 channel PMT as neutron imaging detector. The crystal with a physical dimension of Φ15 × 35 mm², and free crack, colorless and transparent was successfully obtained. The crystal formed a single phase with Cas(BO₃)₂ because no impurity phase was detected using XRD measurement. The crystalline quality was superior to those of μ-PD grown one by XRC analysis. It was due to the condition of crystal growth process. By the transmittance spectrum, Ce-doped crystal showed two absorption band around 275 and 345 nm, which corresponds to the transition from the 4f ground state levels of ⁴F₉₂ and ⁷F₉₂ to Ce³⁺ 5d excited state. Another absorption band around 200-250 nm may be attributed to defects of charge compensation, which is due to Ce³⁺ ion located on the divalent Ca sites. Intense Ce³⁺ 5 d-4f luminescence peak appeared around 400 nm, moreover a remnant of STEs emission peak was observed at 310 nm under excited at α-ray. ²⁴¹Am α-ray excited scintillation decay component was found to be about 330 ns. The results consist with those of μ-PD grown one. The energy resolution of the ²⁴¹Am α-ray irradiated pulse height peak enhanced with the improvement of crystalline quality.

Based on the result of evaluations, we developed an imaging detector combining Ce-doped Cas(BO₃)₂ crystalline array and a 64 channel PMT to test the performance for thermal neutron imaging.

After cutting to size of 5.0 × 5.0 × 1.0 mm wafer and polishing, the crystalline array containing 16 pixels optically couple to a window of position sensitive PMT with the optical grease. The MUSASI beam port in JRR-3 is used as the thermal neutron beam source. In order to cut gamma-ray backgrounds, Pb block of 100 mm thickness was set between the PMT and the beam port. The exposure time to produce the image is around 10 min. Among these 15 min, we can detect approximately 180,000 events. The neutron image clearly obtained by the image reconstruction due to γ-ray background signal separation. In the image profile, the scintillation photons from the scintillator arrays were clearly detected under neutron beam irradiation.

Thus we succeed at development of alternative neutron imager and detector to ³He gas counters by this thesis.
論文審査結果の要旨

中性子シンチレータは、X線やγ線と異なる透過能力を持つため、セキュリティ、医療や資源探査、宇宙・素粒子物理などの非破壊検査・放射線計測分野において今後の利用拡大が期待されている。既存技術としては、中性子との散乱断面積が大きく、且つ、バックグラウンドとなるγ線に対する阻止能が極めて小さいことから、Heガスを用いたガス検出器が利用されている。しかしながら、近年、フロンガスのセキュリティ用に高感度にHeガスの需要が高まり、核輸、価格高騰が世界中で問題となった。そのため、代替となる検出器の開発が急務となり、一方で、未だ代替として全ての要件を満たす中性子シンチレータは見つからない。

本研究は、He中性子検出器の代替候補として、中性子捕獲断面積が大きいPoを含浸したアルカリボーラート系シンチレータ材料の開発を目指し、材料探索から実際のアプリケーションを模擬した中性子イメージング試験までをまとめたもので、全7章からなる。

第1章は、序論であり、本研究の目的と目的および論文の構成に関して述べている。第2章は本研究に関連した先行研究をまとめている。第3章では、実験方法を述べている。本研究においては、捕獲の母結晶としてイットリウムカルシウムオキシカンボレート YCa2(BO3)3、ストロンチウムメタボレート SrB2O4、カルシウムメタボレート CaB2O4及びカルジウムオキシカンボレート CaB2O4の4種類に着目し、これらの母結晶にCe3+をヒストレオトとして希土類元素およびその他の発光中心原子（Pr3+, Bi3+, Cu3+、など）を微量添加したものについて、マイクロ分画下法を用いて単結晶成長を行った。材料探索により、特に優れたものが見つかった後、造粒スクリーニング法により発光の外観を行っても、特に改善を試みた。作製されたサンプルは粉末X線回折により相の同定や、不純物相が生じていないかなどを確認した。研磨されたサンプルは、X線回折スクリーニング法を用いて、ピークの半価幅から結晶性の評価を行った。特に、マイクロ分画下法と造粒スクリーニング法を用いた2つの異なる製法による結晶性の違いについて比較検討した。光学特性評価として、可視域での透過率測定や、シットクルミニサツテストを行い、発光波長に対する透過率や発光中央発光に依る発光不純物の基礎的な光特性について確認した。放射線応答評価では、中性子の照射を模倣したα線照射時の放射特性や蛍光寿命、加えて、アプリケーションの観点からフォトンカウンティングによる放射能スペクトラムの測定を行った。波高値スペクトラムにおいてα線が検出されるものについては、Po核種を用いた中性子応答を評価し、同時に中性子の同定を行った。以上の実験により、特に有用な材料については、造粒スクリーニング法により、中性子イメージング試験を試みた。

第4章、第5章、第6章では、結果と考察を示している。まず、研究対象であるYCa2(BO3)3、SrB2O4、CaB2O4及びCaB2O4の単結晶成長を可能にしている。結晶成長方向及び内部分布の温度制御を最適化することにより、物性特性を測定し、その通じて母結晶としてアルカリボーラート系単結晶の作製技術を確立した。作製された結晶については、粉末X線回折により単相であることを確認するとともに、X線回折スクリーニング測定により結晶性の評価を行い、本研究により用いた結晶が市販の光学結晶と同様の結晶性を有していることを確かめた。光学特性評価においては、透過率測定により各添加元素の吸収が測定域に現れていることを確認して、また、発光波長による基礎的な発光特性を確認した。放射線応答評価および放射能スペクトラムの測定から、単結晶として十分な発光を実現するものとして、Ce3+:CaB2O4及びCe3+:CaB2O4の2種が選出された。産業化の観点から透過性に優れた構造が見つかったが、放射線に対する高反応性に優れたCe3+:CaB2O4が本研究では最も有望な材料であると結論づけた。この結果をもとに、放射性的な光電子増倍管と組み合わせることで中性子検出器を試作した。作製した検出器とJRR-3にによる重視け線中性子実験のMUSASDを用いて、実験に中性子アラームによる実験を試みた。得られた波高値スペクトラムからバックグラウンドノイズを除去し、画像を再構成した結果、中性子によるイメージングを得ることに成功した。これにより、本研究で開発したCe3+:CaB2O4シンチレータが、中性子検出器に一般に用いられる放射能スペクトラムによるフォトンカウンティング型の放射線検出器の現状を示すことができることが確認された。

第7章は、総括であり、本研究で得られた成果を要約している。

以上、要するに本論文は、今後必要とされるHe中性子検出器の代替材料候補となり得る新型アルカリボーラート系シンチレータ材料の探索から実際に検出器としての性能テストをを行い2次元像の取得にも成功したものの、近年のHe資源の枯渇を見据ええた先駆的な研究であるとともに、新たな発展をもたらす研究が期待される。よって、本論文は博士(工学)の学位論文として合格を認める。