Single Crystal Growth and Scintillation Properties of Pr-doped Rare Earth Orthoaluminates for Positron Emission Tomography (陽電子放射断層撮影用Pr添加希土類オルソアルミネートの単結晶成長とシンチレーション特性)

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論文内容要旨

MOTIVATION

This work deals with the development of fast Pr^{3+}-doped oxide orthoaluminate scintillator for potential use as an ionizing radiation detector in modern nuclear medical imaging, i.e. Positron Emission Tomography (PET). This technique plays an increasingly important role in the early diagnosis of cancer and illnesses of the brain such as Alzheimer's decease. Inorganic scintillator single crystals are an integral part of the scanner's design and used for the coincidence detection of 511 keV photons arising from electron-positron annihilation and, finally, to produce an image of the designated area of a human body [1]. In order to improve the detection resolution in time and space, several ideas have been proposed. New ideas require new scintillators and in the last years there have been efforts to develop new scintillating materials that meet the requirements of fast decay time, high light output and high detection efficiency [2]. The most studied systems are mainly Ce^{3+}-doped crystals such as LSO:Ce (currently employed), YAG:Ce, YAP:Ce, LuAP:Ce and others [3]. Recent results of Pr-doped scintillators reveal that analogous to the fast *5d-4f* luminescence of Ce^{3+}, high energy shifted and even faster emission can be obtained from the *5d-4f* transition of the Pr^{3+} in host matrices with the medium-strength crystal field [4]. Scintillators with exceptionally fast timing characteristics are of high priority because they can provide high timing resolution of the detection system. A number of Pr^{3+}-doped scintillators, $Lu_3Al_5O_{12}$, $Y_3Al_5O_{12}$, Y_2SiO_5 and Lu_2SiO_5 have been a subject of interest for potential use in PET [5]. One of them, $YAlO_3$:Pr (YAP:Pr), may appear as a promising scintillator. Mixed crystals $Lu_xY_{1-x}AP$:Pr are even more attractive for PET application due to elevated density that leads to a higher stopping power for γ-rays to be registered in PET scanners.

GOALS AND TASKS

The main objective of the research project is development of Pr^{3+}-doped oxide ortho-aluminate scintillator based on the fast *5d-4f* luminescence for potential use as a γ-ray detector in PET. The strategy and unique point of this work are the use of the micro-pulling-down (μ-PD) method for systematic study and new materials screening by single crystal growth. In order to achieve these goals there are tasks to be solved: 1) Shaped single crystal growth of Pr-doped orthoaluminates YAP and (Lu,Y)AP by the micro-pulling-down method in order to define an optimal composition of the Pr-doped orthoaluminate scintillator possessing a good crystal quality and elevated density; 2) Bulk crystal growth by the Czochralski technique; 3) Crystal as well as optical and scintillation characterization, 4) Optimization of growth parameters and scintillation performance; 5) Detailed study of scintillation mechanism and charge trapping in scintillation kinetics of YAP:Pr scintillator

METHODS

Systematic study and single crystal growth of YAP:Pr and (Lu,Y)AP:Pr were carried out by the micro-pulling-down method [6]. The μ-PD method has an advantage over commercial bulk crystal growth systems, such as Czochralski and Bridgman, since it has the capability to produce single crystalline materials quickly and relatively inexpensively and the grown samples are of sufficient dimensions for all necessary characterization. Therefore, the μ-PD method was chosen as very efficient tool for the systematic study. In all growth experiments oxide powders of 99.99% purity were used as starting materials to prepare stoichiometric mixtures. Crystals were grown from Ir crucible with a square-shaped die heated inductively. N_2 gas atmosphere was used to prevent oxidation of the crucible. YAP [001] oriented single crystal was used as a seed. After finding out of the optimal composition, a set of model crystals was grown using the conventional Czochralski (Cz) growth technique. The study on crystallographic properties as well as growth characteristics and defects was performed. To identify the obtained phase, powder X-ray diffraction analysis was carried out in air at room temperature (RT). The chemical composition and dopant ions concentration and distribution in the grown crystals were analyzed by Electron Probe Micro-Analysis and Inductively Coupled Plasma Atomic Emission Spectroscopy. The suitability of Pr-doped orthoaluminate scintillator for potential use as gamma-ray detector in PET was evaluated on the basis of its scintillation performance. Measurements of photo- and radioluminescence characteristics were performed within 80–300 K using Spectrofluorometer 199S (Edinburgh Instruments). Thermoluminescence (TSL) measurements after X-ray irradiation at RT were performed from RT up to 400 K with. The radioisotope ^{22}Na (511 keV photons) was used to measure scintillation decay. Scintillation light yield was measured using a Hybrid Photomultiplier technique.

MAIN RESULTS AND CONTRIBUTION

This thesis is a systematic study that covers the major aspects of the synthesis and characterization of inorganic single crystal scintillators to be used as γ-ray detector in PET. Single crystals of Pr-doped rare earth orthoaluminates YAP and LuYAP are the main focus of this study.

I. Single crystal growth

1) Single crystal growth of promising Pr^{3+}-doped rare earth orthoaluminate scintillator materials for the application in PET was performed. Crystal growth technology has been established to obtain square-shaped crystals of $YAlO_3$:Pr and $Lu_xY_{1-x}AlO_3$:Pr ($0 \le x \le 0.3$) by the μ-PD method, Fig. 1. The bulk scintillator crystals of optimal composition were grown by the conventional Cz technique, Fig. 2. The results of single crystal growth, phase homogeneity, axial dopant distribution, and crystallinity allow considering crystals obtained to be of reasonable quality for optical characterization.

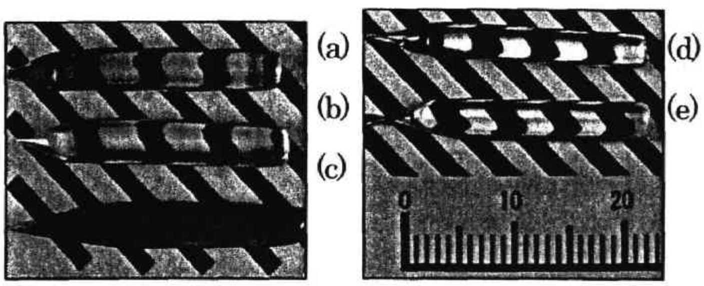

Fig. 1. Square-shaped crystals growth by the μ-PD method: YAP – (a), YAP: Pr(0.5%)– (b), YAP:Pr (0.5%) co-doped with Si 200 ppm – (c), Zr 200 ppm – (d) and Mo 0.05% – (e). Scale is given in mm

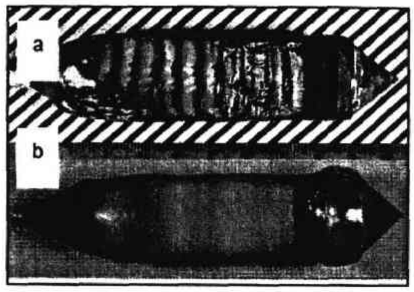

Fig. 2. Mixed crystals $Lu_xY_{1-x}AP$:Pr (1 mol%), $x = 0.1$ – (a) and $x = 0.3$ – (b) (nominal composition) grown by the Cz technique

2) YAP:Pr was explored towards optimization its scintillation performance for specific application in PET. Scintillation performance can be often degraded due to electron localization at trapping states that is usually the reason of delayed recombination at luminescent center. Co-doping with optically inactive aliovalent ions is known to be effective to overcome this trouble [7]. So far, charge trapping mechanism in YAP:Pr has not been identified; therefore we applied an approach of co-doping with tetra- and trivalent ions to reduce the concentration of shallow and deep active traps. Unique screening capability of the μ-PD method was successfully applied for systematic study and crystal growth of YAP:Pr co-doped with tetravalent (Zr^{4+}, Si^{4+}, Hf^{4+}) and trivalent (Ga^{3+}, Mo^{3+}) ions of selected concentrations (~50-1000 ppm), Fig.1. This work is the first attempt to improve scintillation performance of YAP:Pr by applying the co-doping schemes.

II. Characterization of scintillation properties

1) To meet the goal of this research work, suitability of YAP:Pr and (Lu,Y)AP:Pr scintillators for potential use as gamma-ray detector in PET has been evaluated. Radioluminescence intensity proves an efficient

energy transfer from the hosts to Pr^{3+} center. Steady-state scintillation efficiency can approach that of Ce-doped YAP for the optimized Pr concentration (0.3-0.5%) and exceeds that of BGO ~10 times. Scintillation decay is very fast; however the approximation shows a two-exponential pattern with the ~9 ns decay time in the fast component and a few hundreds ns decay time in the slower component.

2) Particularly interesting novel approach of co-doping (Zr^{4+}, Si^{4+}, Hf^{4+}) and (Ga^{3+}, Mo^{3+}) appears rather contraproductive. Addition of trivalent ions into YAP:Pr induces peaks of parasitic absorption in 280-320 nm spectral range and co-doping with tetravalent ions results in 400 nm absorption bands, which can be ascribed to F^{+}-centers, and Pr^{4+} or O^{-} hole centers, respectively. Rather significant decrease of Pr^{3+} *5d-4f* luminescence intensity and relative enhancement of *4f-4f* emission lines was found under X-ray excitation. Similar effect is observed because of concentration quenching at high (above 1 mol%) Pr concentration in Pr-only doped YAP. It may point to pairing "Pr + codopant" or "Pr + Pr" ions.

III. Study on scintillation mechanism

1) Since the development of scintillators requires good understanding of the scintillation mechanism, detailed analysis along with an in-depth discussion of results was needed. We studied capture of migrating electrons and holes in YAP:Pr scintillator by the TSL and proposed a simple model describing these phenomena with respect to shallow traps. Unusual TSL glow curves point to possible interplay between Pr^{3+} and surrounding oxygen ions in the localization of holes. Hole becomes localized at oxygen ligands and electron possibly at Pr ion, i.e. a complex "O^{-} + Pr^{2+}" can be created as a result of charge carrier capture (creation of complex "O^{-} + Pr^{3+} + VO•" can not be excluded as well).

2) Complicated charge trapping mechanism appears disadvantageous to obtain fast scintillation response together with high light yield. The RT decay (de-trapping) time of O^{-} center related to TSL peak at 185 K is estimated of the order of 1 ms, about one order longer with respect to electron trap related to 110 K peak in YAP:Ce. Thus, delayed recombination at Pr^{3+} center extends still to longer times and this feature could explain rather low photoelectron yield achieved in comparison with YAP:Ce.

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論文審査結果の要旨

Pr^{3+}を発光中心とするパリティ許容遷移に伴う発光を利用したシンチレータは、現在、PET 用に最も用いられている Ce^{3+}系シンチレータに比して蛍光寿命が短く、高発光量が期待できる点が特徴であり、Pr:LAG 等の酸化物結晶において注目され始めている。この Pr^{3+}のパリティ許容遷移に伴う発光は、Pr^{3+}の 5d 順位と母結晶の $^1S_0$順位との位置関係に大きく依存し、特定の条件を満たさない限り発光は観察されないとされている。しかしながら、これまで母結晶と Pr^{3+}の 5d-4f 遷移に起因する発光の関係における系統的な研究はなされていない。

本研究は、Pr^{3+}の 5d-4f 遷移に起因する発光が希土類オルソアルミネートを母結晶とした際にどの様な挙動を示すかをまとめたもので、全 4 章からなる。

第 1 章は、序論であり、本研究の背景と目的を述べている。

第 2 章では、実験方法を述べている。本研究においては、研究対象の Pr^{3+}添加希土類オルソアルミネートを研究する際、まず、$YAlO_3$を母結晶としてマイクロ引下げ法により異なる Pr^{3+}の組成比を変えたものの単結晶成長を行った。また、母結晶から発光中心へのエネルギー伝搬の際に欠陥に捕獲される確率を減らすことで、発光効率を向上させることを狙い、4 価のイオン (Hf^{4+}, Zr^{4+}, Si^{4+})、3 価のイオン (Mo^{3+}, Ga^{3+}) 等の添加を試みた。母結晶を高密度化する観点からは、Y のサイトを Lu で置換することを行った。メカニズム等の議論に重要な役割を果たす組成に関しては、引き上げ法により高品質単結晶を作製した。粉末 X 線回折法により相を同定することで固溶域を調べ、各種イオンの組成分布は電子線マイクロプローブ分析装置 (EPMA) にて測定した。紫外から可視域による吸収、紫外線励起による発光の測定に加え、X 線励起および γ 線励起によるシンチレーション特性も行った。また、点欠陥のマクロな評価として熱蛍光測定も行った。

第 3 章では、結果と考察を示している。まず、研究対象である Pr^{3+}添加希土類オルソアルミネート単結晶成長を可能にしている。結晶成長方法は、材料探索の観点から高速の結晶作製方法としてマイクロ引下げ法を、物性測定を厳密に行うため高品質単結晶を作製する観点から引上げ法をそれぞれ選択し、その結晶成長方向の温度勾配を適切に設定するなどすることで Pr^{3+}添加希土類オルソアルミネート単結晶の成長方法を確立した。

また、EPMA により作製した結晶における添加物の分布を、結晶の径方向、結晶成長方向の両方向において調べた。X 線ロッキングカーブにより結晶性を評価し、本研究に用いた結晶が市販の光学結晶と同等の結晶性を有していることを確かめた。シンチレーション特性に関連する光学特性評価も行った。紫外から可視域による吸収により Pr^{3+}の 5d の吸収の有無を確認し、紫外線により Pr^{3+}の 5d 準位を直接励起することで、5d-4f 遷移に起因する発光を測定した。結晶をシンチレータとして使用する場合、放射線からのエネルギーを母結晶で吸収した場合も同様の発光が（短寿命で）起こる必要がある。そこで、本章ではシンチレーション特性評価として、X 線励起および γ 線励起においても、5d-4f 遷移に起因する発光を確認した。その結果、長寿命発光成分が多いことが分かり、母結晶から発光中心へのエネルギー伝搬の際に欠陥に捕獲されていると考えた。点欠陥は電子を捕獲し、蛍光寿命を長くしてしまう原因となるため、この現象を説明するために、点欠陥量のマクロな評価として熱蛍光測定も行い、長寿命成分の原因が点欠陥に起因することを示した。そこで、この欠陥に捕獲される確率を減らすことで、発光効率を向上させることを狙い、4 価のイオン (Hf^{4+}, Zr^{4+}, Si^{4+})、3 価のイオン (Mo^{3+}, Ga^{3+}) 等の添加を試みた。いずれの添加物の場合も発光効率を向上には結び付かなかったが、そのメカニズムを検討し、モデルを構築した。また、母結晶を高密度化する観点からは、Y のサイトを Lu で置換することを行った。

第 4 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、結晶性の高い Pr^{3+}添加希土類オルソアルミネート結晶の融液からの単結晶成長方法を確立することによって、希土類オルソアルミネートを母結晶とした場合の Pr^{3+}の 5d-4f 遷移に起因する発光を研究したもので、最近注目されている Pr^{3+}系をはじめとする新規シンチレータ開発の発展に寄与するところが少なくない。よって，本論文は博士(工学)の学位論文として合格と認める。