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論文内容要旨

[1. INTRODUCTION]

Scintillators emit light in ultra violet, visible and infrared regions of electromagnetic spectra by converting ionizing radiation (for example, α-ray, β-ray, γ-ray, X-ray, or neutrons) into a number of photons. Many types of inorganic scintillating materials including oxides, fluorides, bromides, iodides, and chlorides are widely produced and examined in terms of both practical applications and academic research. These materials are used in various applications ranging from nuclear medicine (PET, X-ray CT, and SPECT), basic scientific research, geophysical exploration (mineral and oil), land mine exploration, atomic energy (nuclear fusion), earthquake prediction, to security field. Until now, utilization of scintillators in nuclear medicine came into the spotlight. However, after 9/11 terrorist attacks, demand in security fields including baggage inspection in airports and homeland security is continuously increasing. Furthermore, after the Great East Japan Earthquake of 2011, the demand for scintillators as sensors of ionizing radiation increased considerably in order to detect radioactive isotopes in food or environment including architectural structures and air.

This research project was focused on three sesqui-oxide materials including Y_2O_3, Sc_2O_3, and Lu_2O_3. First motivation point for this study was related to deficit of knowledge on scintillation properties of these materials, because single crystal growth of these sesqui-oxides is difficult due to high melting point around 2400℃. Therefore, initial reports of scintillation properties for these materials have significantly scientific meaning. In the second place, efficient γ-ray scintillators require high effective atomic number (Z_{eff}) and high density that are responsible for probability of photoelectric effect and γ-ray stopping power, respectively. Z_{eff} and density of Y_2O_3 and Lu_2O_3 are higher than those of representative scintillators Ce:$YAlO_3$ (YAP), Ce:$Y_3Al_5O_{12}$ (YAG), and Ce:Y_2SiO_5 (YSO). It means that Y_2O_3 and Lu_2O_3 are expected to be excellent γ-ray scintillators. As a final point of motivation, fabrication methods of transparent ceramics are establishing using special equipments, especially, since Y_2O_3, Sc_2O_3, and Lu_2O_3 have cubic symmetry and do not show optical anisotropy, high transparency ceramics can be relatively easily fabricated compared to other compounds with no cubic structure. Therefore, these three oxides were selected as research object. The research objectives of this study were synthesis of Y_2O_3, Sc_2O_3, and Lu_2O_3 single crystals and transparent ceramics, evaluation and comparison of their scintillation properties, and discussion regarding relationship between light yields and defects based on ascription of emissions.

[2. EXPERIMENTAL]

The single crystals were grown by the micro-pulling-down method. Transparent ceramics were fabricated by vacuum sintering and Spark Plasma Sintering (SPS) technique.

To evaluate surface properties and chemical composition, scanning electron microscope (SEM, FE-SEM) and energy dispersive X-ray analysis (EDX) measurements were carried out. Structural perfection of the crystals was inspected using full width at half maximum (FWHM) of X-ray rocking curves. Density and crystal grain size of the ceramics were calculated by Archimedes method and Mendelson method, respectively.

The optical transmittance was measured in the range of 200-800 nm. Radio-luminescence spectra were evaluated by attaching the samples on the surface of a ^{241}Am α-ray source and following detection of emitted signal by spectrofluorometer.

The γ-ray scintillating properties were characterized using the pulse height spectra, the light yield, the non-proportionality, the energy resolution, and the decay kinetics. The pulse height spectra under γ-ray excitation were examined with a bias photomultiplier tube (PMT) operating at high voltages and by attaching the samples on the PMT window with optical grease. The PMT output signal was fed to a shaping amplifier with shaping times of 0.5 μs and 2 μs and a multichannel analyzer. The resulting signal was stored on a personal computer. The γ-ray excited scintillation decay courses were obtained through a PMT and by using a digital oscilloscope directly.

[3. RESULTS –Growth and Fabrication-]

Y_2O_3, Sc_2O_3, and Lu_2O_3 single crystals were grown by the micro-pulling-down method using Re crucible as a melt container and ZrO_2 ceramic as a heat insulators in $Ar+H_2$ (3%) gas flow to prevent Re from oxidation. First Y_2O_3 crystal growth was performed on commercial Y_2O_3 ceramic rods as a seed, and first Sc_2O_3 and Lu_2O_3 crystals were grown on W wire (as a seed). Thereafter, the grown crystals or solids were used as seeds to obtain good quality crystal. Transparent ceramics were fabricated by vacuum sintering from fine precursor powder synthesized at low temperature and Spark Plasma Sintering (SPS). In the case of SPS specimens, the as sintered materials were grey or black due to presence of oxygen vacancies. Therefore, the SPS sintered compacts were annealed in air for 12 hours at 1000-1100℃.

The FWHM of rocking curves for Y_2O_3, Sc_2O_3, and Lu_2O_3 single crystals were evaluated to be about 116arcsec, 111arcsec, and 248arcsec (222 reflections), respectively. Relative densities of the transparent ceramics were estimated to be approximately 99.4% (Y_2O_3 ceramics by vacuum sintering), 99.37% (Y_2O_3 ceramics by SPS), 99.39% (Sc_2O_3 ceramics by SPS), and 99.74% (Lu_2O_3 ceramics by SPS), respectively. Average crystal grain size of the transparent ceramics were calculated to be 43μm (Y_2O_3 ceramics by vacuum sintering), 0.468μm (Y_2O_3 ceramics by SPS), 2.36μm (Sc_2O_3 ceramics by SPS), and 0.91μm (Lu_2O_3 ceramics by SPS), respectively.

[4. RESULTS –Y_2O_3-]

According to previous reports, the nature of emission peaks for sesqui-oxides including Y_2O_3 is not well understood. To determine origin of the emission peaks, the photo-luminescence measurements were performed under band to band excitation at 8K to 490K. First, self trapped exciton (STE) emission is intrinsic emission of the material. Generally speaking, STE emission can be observed under band to band excitation at extremely low temperature similar to 8K. Second, F^+ center emission can be only observed in the materials containing oxygen vacancies. Another possible origin of emission peaks is trapped exciton (TE). TE emission is annihilation of electrons and holes that are trapped at some defect (even though defect is not exactly identified). When Y_2O_3 crystal was excited by 195 nm corresponding to band to band excitation, 260 nm emission peaks (STE) were observed, and the peak was discovered for the first time in this material. On the other hand, the emission peaks observed for Y_2O_3 ceramics that contained many defects were associated with STE (260 nm and very weak), TE (360 nm), and oxygen vacancies (over 400 nm) under band to band excitation.

Considering the radio-luminescence spectra recorded under ^{241}Am α-ray irradiation, Y_2O_3 crystal emitted at 350 nm and Y_2O_3 ceramics (both vacuum sintering and SPS) emitted at 350 nm. From pulse height spectra obtained under ^{137}Cs excitation, light yields were calculated to be approximately 1300±130 ph/MeV (for the crystal), 9300±930 ph/MeV (for vacuum sintered ceramic), and 5100±150 ph/MeV (for SPS ceramic), respectively (Fig. 1). These results were reported together with the pulse height spectra for the first time.

From non-proportionality plots that mean relative light

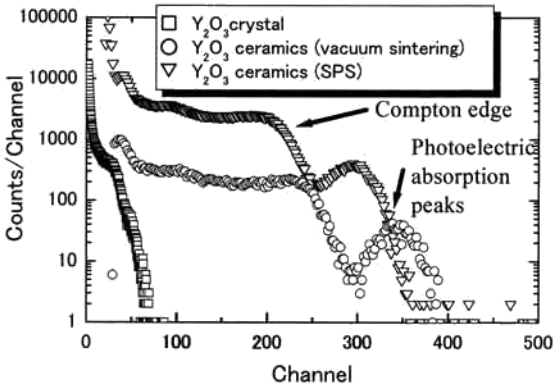

Fig. 1. Pulse height spectra of Y_2O_3 under ^{137}Cs excitation.

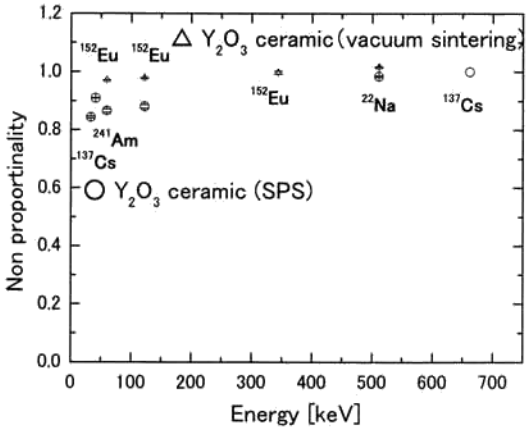

Fig.2. Non-proportionality plots of Y_2O_3 using various γ-rays emitters.

yields (LY) by reference to ^{137}Cs peak, Y_2O_3 ceramics demonstrated good proportionality (Fig. 2). It indicates that scintillation yield is almost constant for different sources. Unfortunately, non-proportionality for the crystal could not be plotted.

Energy resolutions under the ^{137}Cs excitation were estimated to be approximately 18% (vacuum sintering) and 25% (SPS), respectively (Fig. 3). Slopes of fitting were estimated to be -0.29 (for vacuum sintering) and -0.33 (SPS). Since peak broadening of energy resolution obey statistical fluctuation, theoretical slope in fitting should be -0.5. However, due to non-statistical factor including non-uniformity of the ceramics or properties of PMT or non-perfect reflectivity, slope became gentle.

The scintillation decay was fitted by fast component of about 34 ns (15%) and a slower one of about 107 ns (85%) for the Y_2O_3 ceramic produced by vacuum sintering, and fast component of about 16 ns (26%) and a slower one of about 70 ns (74%) for the Y_2O_3 ceramic produced by SPS.

Y_2O_3 ceramics demonstrated excellent γ-ray response in terms of LY, non-proportionality, and decay kinetics.

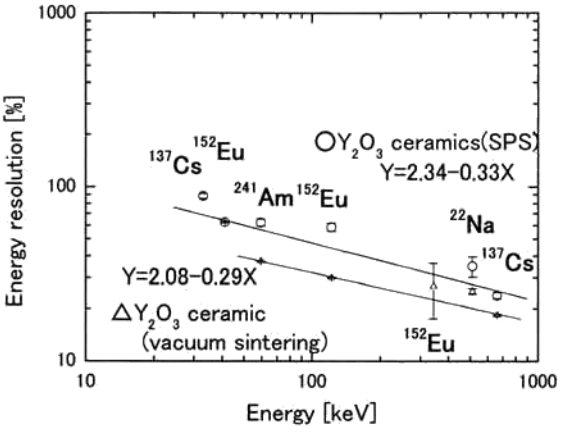

Fig.3. Energy resolution plots of Y_2O_3 ceramics using various γ-rays emitters.

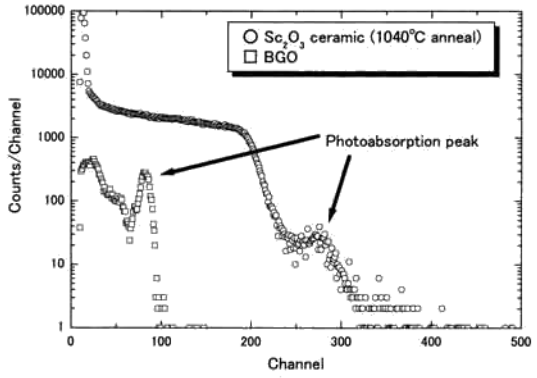

Fig.4. Pulse height spectra of Sc_2O_3 ceramic under ^{137}Cs excitation together with BGO data as a reference.

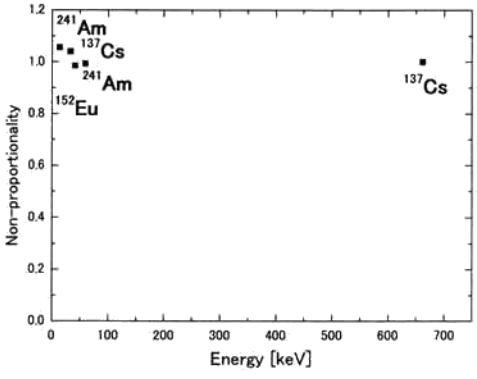

Fig.5. Non-proportionality plots of Sc_2O_3ceramic using various γ-rays emitters.

[5. RESULTS –Sc_2O_3-]

Sc_2O_3 single crystal emitted at 240 and 260 nm that are assigned to STE under band to band excitation at low temperature. These results were observed for the first time. As for the Sc_2O_3 ceramic spectra, the emission derived from TE was dominant that is consistent with previous reports. According to previous papers, origins of these peaks were not evident. However, our results demonstrated that emission at 350 nm can be associated with TE.

The LY of Sc_2O_3 crystal and ceramic were approximately 5500±550 ph/MeV (non-annealed) and 20000±2000 ph/MeV (annealed) (Fig. 4). Moreover, the Sc_2O_3 ceramic has good proportionality (Fig. 5). However, due to non-uniformity of the ceramic, the photo-absorption peaks under ^{55}Na (511keV) and ^{152}Eu (122keV, 344keV) excitations cannot be measured. As a result, non-proportionality figure is not perfect.

Energy resolutions under ^{137}Cs excitation were estimated to be approximately 17% (SPS). Slope of fitting was estimated to be about -0.4 (SPS). Similar to the Y_2O_3 ceramics, due to non-statistical factor, slope did not become steep (Fig. 6).

The scintillation decay of Sc_2O_3 was fitted by fast component of about 45 ns (29 %) and a slower one of about 271 ns (71%) for Sc_2O_3 single crystal. The fast component of about 64 ns (8%) and a slower one of about 295 ns (92%) were observed for the Sc_2O_3 ceramic fabricated by SPS and annealed at 1040℃.

Since Sc_2O_3 has low Z_{eff} and low density, this material was not considered as γ-ray scintillators in the past. However, this thesis demonstrated that Sc_2O_3 ceramic has excellent γ-ray response in terms of LY. It should be noted that the LY of Sc_2O_3 ceramic is comparable to those of representative scintillators Ce:YAG, Ce:YSO, and Pr:$Lu_3Al_5O_{12}$ (LuAG).

[6. RESULTS –Lu_2O_3-]

Two emission peaks (around 260 nm and 390 nm) of Lu_2O_3 were reported in the past, and origin of these emissions was explained differently. In this report, emission peaks of Lu_2O_3 around 235 nm and 275 nm are assigned to STE under band to band excitation, and emission around 390 nm is assigned to trapped exciton (TE). These new findings clarify emission mechanisms of sesqui-oxides that were not well described in previous reports.

Origin of emission peaks for Lu_2O_3 ceramic around 390 nm under ionizing radiation excitation was determined as trapped exciton (TE) together with the peaks associated with Tb^{3+} impurity contained in the starting powder. However, since emission energy flow emission of Tb^{3+} impurity, TE emission of Lu_2O_3 became very weak, therefore, photo-absorption peak of Lu_2O_3 can not be observed.

Considering Z_{eff} and density, Lu_2O_3 is assumed to be the most promising γ-ray scintillator in among three oxides, but, as it is shown in this report, scintillation characteristics of Lu_2O_3 can not be evaluated accurately due to impurity emission.

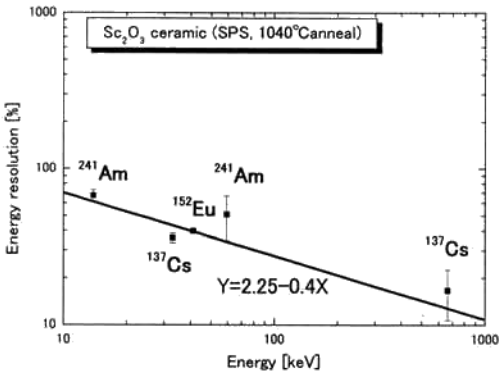

Fig.6. Energy resolution of Sc_2O_3 ceramic using various γ-ray emitters

[7. DISCUSSION and 8. GENERAL OVERVIEW]

Obtained results demonstrated that the LYs of Y_2O_3 and Sc_2O_3 ceramics were considerably greater than those of corresponding single crystals. Additionally, Y_2O_3 and Sc_2O_3 ceramics have sufficiently excellent γ-ray characteristics in terms of LY, proportionality, decay kinetics, and hygroscopic when compared to other representative scintillators. Furthermore, correlation between the LY and defects was discussed, and improvements of scintillation properties after annealing treatment were experimentally confirmed.

論文審査結果の要旨

本研究は、Y_2O_3, Sc_2O_3, Lu_2O_3 単結晶と透明セラミックスの作製とそれらのシンチレーション特性を評価し比較をまとめたもので、8章からなる。

第1章は序論である。研究対象とした Y_2O_3, Sc_2O_3, Lu_2O_3 は融点が2400℃近辺であり、既存の単結晶育成方法ではメルトからの育成は難しいこと、また透明セラミックスも様々な方法で作製が試みられているが依然として作製が容易ではないこと、更にこれらの材料にシンチレータの代表的な発光中心である Ce や Pr を添加しても photoionization によって発光しないことを説明した。無添加 Y_2O_3, Sc_2O_3, Lu_2O_3 のシンチレーション特性はまだ十分に解明されておらず、単結晶とセラミックスの比較研究も未だに十分に研究されていないため、これらを解明することを本研究の目的とした。

第2章及び第3章において、実験方法を述べた。合成系としては、マイクロ引下げ法による単結晶合成、真空焼結及びススパークプラズマ焼結による透明セラミックスの作製に関して説明し、表面・組成分析、バンド端励起による発光ピークの帰属方法、放射線応答の実験系を説明した。

第4章では、Y_2O_3 単結晶とセラミックスのシンチレーション特性を明らかにした。8K の低温でバンド端励起による発光スペクトルを測定し発光ピークの帰属を決定したところ、単結晶サンプルから、250nm 近辺に自己束縛励起子由来の発光ピークを世界で初めて測定するに至った。同時に、過去文献から自己束縛励起子発光と考えられていたピークが欠陥由来の束縛励起子発光だと結論づけられ、かつ酸素欠損由来の発光スペクトルも確認した。これらの結果はセスキオキサイド材料の発光メカニズムを研究する上で新たな知見と言える。シンチレーション特性を評価したところ、双方に 350nm にピーク中心を持つ欠陥由来の radio-luminescence を観測した。^{137}Cs 励起下での発光量は単結晶が 1300ph/MeV、セラミックスが 9300ph/MeV になることが明らかになった。線源毎の相対発光量である non-proportionality はセラミックスにのみプロット可能で良好な proportionality を示した。放射線弁別能であるエネルギー分解能は 18.4%（セラミック）で、改善の必要性がある。□/□比は□□□□（セラミック）と評価できた。Scintillation decay は 34ns(15%)と 107ns(85%)（セラミック）と評価でき、高速応答を示すことが分かった。Y_2O_3 サンプルでは、単結晶よりもセラミックが優れた□線応答を示すという知見を得た。

第5章では、Sc_2O_3 を中心に研究成果を報告した。バンド端励起による発光スペクトルを調べたところ、250nm 近辺に世界で初めて自己束縛励起子による発光を確認した。単結晶とセラミック共に 340nm にピーク中心を持つ欠陥由来の radio-luminescence を観測した。発光量は単結晶が 5500ph/MeV、セラミックが 20000ph/MeV と見積もれ、特にセラミックは代表的なシンチレータの発光量に匹敵する高発光量を示したのは大きな発見である。Non-proportionality は良好な proportionality を示した。エネルギー分解能は 16.7%（セラミック）と改善の必要性がある。Scintillation decay は 64ns(8%)と 295ns(92%)（セラミック）であったが、一方かなりの長残光も示した。また単結晶を 900℃、空気中でアニール処理を行い酸素欠損サイトに酸素を補充すると、発光量は 8000ph/MeV と改善されるという知見を得た。Sc_2O_3 サンプルでも単結晶よりもセラミックが優れた□線応答を示すという知見を得た。

第6章では、Lu_2O_3 を中心に研究成果を報告した。バンド端励起による発光スペクトルを測定すると、過去文献と同じ波長領域に自己束縛励起子発光を観測した。また 390nm にピーク中心を持つ欠陥由来の radio-luminescence を観測した。しかしながら、□線応答特性を評価するに至らなかった。この材料は高密度かつ高有効原子番号であるために、当初最も優れた□線応答を示すと予想したが、原料粉末に完全に分離しきれなかった Tm イオンが混じっており、発光のエネルギーが Tm 発光に流れてしまい材料の発光によるシンチレーション特性を正確に評価できなかったと結論づけた。

第7章は得られた実験結果に基づいた議論を行った。また、欠陥と発光量の相関関係を調べ、特に、セラミックスサンプルの発光量の差は何が原因で起こるのかの検討を行なったところ、結晶粒径（欠陥を評価するために導入）と発光量の間には密接な関係があり、結晶粒径が大きくなるほど発光量が増大することを明らかにした。

第8章では、まとめを行った。主な成果として「Y_2O_3, Sc_2O_3, Lu_2O_3 単結晶と透明セラミックスの作製に成功したこと」、また「工業化を行えるほど、マイクロ引き下げ法によるセスキオキサイド単結晶の育成プロセスを精査したこと」、「バンド端励起によるセスキオキサイド材料の発光ピークの帰属に成功しこれらの材料の発光特性を調べるうえで大きな知見を得たこと」、さらに「今まで十分に研究されていなかった Y_2O_3, Sc_2O_3, Lu_2O_3 単結晶の□線応答を詳細に調べたこと」、「Y_2O_3, Sc_2O_3, Lu_2O_3 セラミックスの□線応答の評価に成功しそのうち Y_2O_3 と Sc_2O_3 は、発光量と non-proportionality, scintillation decay の観点から、既存のシンチレータに匹敵する優れた□線応答を示すという知見を得たこと」、「透明セラミックスが□線シンチレータとして大きな可能性を有していることを確認したこと」、「新規セスキオキサイドシンチレータを発見したこと」、「セラミックスの結晶粒径と発光量の関には密接な関係がある」ことを明らかにしたことなどが挙げられる。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。