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学位論文題目	Crystal Growth and Optical Properties of Garnet-type Oxide Scintillation Crystals with Near Infrared Emission
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論文内容要約

Scintillators are materials that convert high energy radiation such as α -ray, β -ray, γ -ray, neutrons, and heavy ions into a large number of lower energy photons. They are widely used for radiation detection in various technical fields such as high energy physics, security control, and medical imaging. Most scintillators emit the scintillation light in the wavelength range from ultra-violet to visible region (from 200 to 600 nm) that often corresponds to sensitivity range of the optical detectors. Recently, scintillators demonstrating emission in the infrared range have received much attention because novel silicon based detectors with high quantum efficiency in the infrared range have been developed. Therefore, the scintillator applications using the unique features of the infrared region have been investigated. In previous studies of scintillators with near infrared emission, noble gases such as Ar and Xe, scintillating powders, and a few bulk crystals such as CsI(Tl) and Yb:Y₃Al₅O₁₂ have been examined. The guidelines for the material design of scintillators with near infrared emission are not determined. Studies of near infrared scintillation bulk crystals are in their early phase. Additional research is necessary to accelerate development of this novel application. The purpose of this thesis is the development of scintillators with near infrared emission. Examination of following five problems was considered as main goal of the current research. (1): To establish light yield measurements for scintillators with near infrared emission. The light yield of the scintillators with near infrared emission was estimated using the imaging method. (2): To perform the systematic material research on the scintillators with near infrared emission. The Cr- or Ti-doped (Gd_{1-y}Y_y)₃(Ga_{1-x}Al_x)₅O₁₂ compounds were systematically sintered and evaluated. (3): To reveal the relationship between the light yield and its parameters in garnet-type oxide scintillators with near infrared emission. The light yield, the band gap, and the quantum yield of Cr- or Ti-doped (Gd_{1-y}Y_y)₃(Ga_{1-x}Al_x)₅O₁₂ were evaluated. (4): To understand the relationship between the emission wavelength and its parameters in garnet-type oxide scintillators with near infrared emission. The emission wavelength and lattice constants of Ti-doped (Gd_{1-y}Y_y)₃(Ga_{1-x}Al_x)₅O₁₂ and alkaline earth metal substituted Gd₃Ga₅O₁₂ were evaluated. (5): To perform the transmission experiments for the meat using high efficient scintillator developed in this study.

As a first step, research of garnet oxide compounds was performed using solid state synthesis. The required solid state polycrystalline materials were fabricated in conventional electric furnace. In this study, the garnet compositions of $(\text{Gd}_{1-y}\text{Y}_y)_3(\text{Ti}_{0.005}(\text{Ga}_{1-x}\text{Al}_x)_{0.995})_5\text{O}_{12}$, $(\text{Gd}_{1-y}\text{Y}_y)_3(\text{Cr}_{0.005}(\text{Ga}_{1-x}\text{Al}_x)_{0.995})_5\text{O}_{12}$, $(\text{Gd}_{1-z}\text{M}_z)_3((\text{Ti}_{0.005}\text{Ga}_{0.995})_{5-3z}\text{Zr}_{3z}\text{O}_{12})$ and $(\text{Gd}_{1-z}\text{M}_z)_3((\text{Cr}_{0.005}\text{Ga}_{0.995})_{5-3z}\text{Zr}_{3z}\text{O}_{12})$ ($x = 0, 0.25, 0.50, 0.75, 1.00$, $y = 0, 0.25, 0.50, 0.75, 1.00$, $z = 0, 0.05, 0.10, 0.20, 0.50$, $M = \text{Mg, Ca, Sr, Ba}$) were prepared by the sintering method. The materials produced in this way were used for the powder XRD analysis and radioluminescence characterization. As the second step, oxide garnet single crystal samples were produced by the micro-pulling down (μ -PD) method. Bulk crystalline sample were especially used for the band gap and light yield measurements. Optical band gap was estimated from transmittance spectrum fitting. Undoped crystals were used for the transmittance spectra measurements because the dopant would have the absorption that overlaps the absorption edge. The sample was kept at 8 K with liquid helium to suppress lattice vibration. In this work, the light yield was estimated from the integration of the emission by using a CMOS camera and alpha-ray excitation. Considering distribution of the dopants, the intensity sum of the square area. The light yield was obtained from the mean value of the intensity sum subtracted the background noise. The relative light yield was estimated by comparison with those values. Transmission experiments using meat were performed to inspect applicability of the newly developed infrared scintillators in practical dosimetry. According to the results of the previous optical evaluations, the Cr 0.1%: GGG crystal was selected to be used as the sample crystal. As a reference sample, an Cr: α - Al_2O_3 ceramics was used.

Considering application of the alpha-ray imaging for the light yield measurements, the light yield from the alpha-ray imaging was compared with that from the general single photon counting method. Gd_2SiO_5 (GSO) crystals doped with 0.5, 1.0, and 1.5% Ce, and Zr co-doped Gd_2SiO_5 (GSOZ) crystals doped with 1.0 and 1.5% Ce were used as sample crystals. In the light yield measurement by alpha-ray imaging, the light yield was estimated from the intensity sum in the same area. Pearson's correlation coefficient between both light yield was calculated to be 0.90. Alpha-ray imaging method was applied to the light yield measurements in place of single photon counting method.

The Cr^{3+} doped garnets shows the mixed luminescence of sharp peaks associated with the $\text{Cr}^{3+} {}^2\text{E} \rightarrow {}^4\text{A}_2$ transition and broad luminescence derived from $\text{Cr}^{3+} {}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ transition under X-ray excitation. The crystal field strength and the bond length between a center ion and ligand atoms have the correlation equation. The lattice constant correlates with the bond length. Thus, the lattice constant and the crystal field strength are also correlated. ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ transition becomes more dominant than ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition when the lattice constant increases. The Cr^{3+} doped garnets shows a broad emission due to the $\text{Ti}^{3+} {}^2\text{E} \rightarrow {}^2\text{T}_2$ transition under X-ray excitation. The emission peak position increased with an increasing in the lattice constant. This result corresponded to the slope of the ${}^2\text{E}$ line in the energy diagram.

The Cr 0.1%:GGG crystal was used to estimate the dose from the light yield under low dose X-ray irradiation. The relative

light yields of nominally Cr 0.1%, 0.5%, and 1.0% doped GGG crystals as a function of Cr concentration was measured. The Cr 0.9%:GGG (nominally Cr 0.1% doping) demonstrated the highest light yield. The relative light yield of the $(\text{Gd}_{1-y}\text{Y}_y)_3(\text{Cr}_{0.005}\text{Ga}_{0.995})_5\text{O}_{12}$ ($y = 0, 0.25, 0.5, 0.75$ and 1.00) garnet crystals was measured to understand the relationship between the band gap and the light yield. The value of the correlation coefficient was 0.20. There is no correlation between the light yield and the band gap in the $(\text{Gd}_{1-y}\text{Y}_y)_3(\text{Cr}_{0.005}\text{Ga}_{0.995})_5\text{O}_{12}$. The value of the correlation coefficient of relative light yield and the quantum yield was 0.03. No correlation between the light yield and the band gap in $(\text{Gd}_{1-y}\text{Y}_y)_3(\text{Cr}_{0.005}\text{Ga}_{0.995})_5\text{O}_{12}$ was detected. The relative light yields of the 0.5%, 1%, and 2% Ti-doped GGG crystals were also measured in the identical conditions. However, their light yield was below detectable limits.

As for $(\text{Gd}_{1-x}\text{M}_x)_3(\text{Cr}_{0.005}\text{Ga}_{0.995})_{5-3x}\text{Zr}_{3x}\text{O}_{12}$ compounds, the emission peak shifted toward longer wavelength when the lattice constant increased. For the $(\text{Gd}_{1-x}\text{M}_x)_3(\text{Ti}_{0.005}\text{Ga}_{0.995})_{5-3x}\text{Zr}_{3x}\text{O}_{12}$ compounds, the emission peak shifted toward longer wavelength with increasing the lattice constant as well as for the $(\text{Gd}_{1-y}\text{Y}_y)_3(\text{Ti}_{0.005}(\text{Ga}_{1-x}\text{Al}_x)_{0.995})_5\text{O}_{12}$ compounds. The band gaps of the garnet-type oxide crystals produced in this study was narrower than that of $\alpha\text{-Al}_2\text{O}_3$. GGG(M,Zr) had narrower band gap than that of GGG, and the light yield of the GGG(M,Zr) was measured. The relative light yield of the Cr 0.1%:GGG(M, Zr) was lower than half of that of Cr 0.1%:GGG. The quantum yield of the Cr 0.1%:GGG(M, Zr) and Cr 0.1%:GGG crystals was within the range from 80% to 85%. The difference of the relative light would be caused by a decrease of quantum efficiencies of the transport of thermalized pairs to the luminescence centers and generation of the defect levels. From the results of the optical evaluation, Cr 0.1%:GGG crystal had the highest light yield and the emission peak at around 730 nm. Thus, Cr 0.1%:GGG was demonstrated to be very efficient scintillator for application in real time-dose monitoring system by using infrared emission scintillator. Cr 0.1%:GGG crystal was used for the transmission experiment by using the meat.

A Cr 0.1%:GGG crystal was used for the transmission experiment using actual pork meat. The infrared emissions from the Cr 0.1% GGG successfully transmitted the meat samples with thickness up to 50 mm. Under the same conditions, radioluminescence spectra of the Cr: $\alpha\text{-Al}_2\text{O}_3$ ceramic were measured. The integrated intensity of the emission from Cr 0.1%:GGG crystal was approximately 3.5 times greater than that from the Cr: $\alpha\text{-Al}_2\text{O}_3$ ceramic. The light yield of the Cr 0.1%:GGG crystal had highest value among Cr doped oxide scintillators with infrared emission. To observe variation of the intensity against the dose received by the scintillator, the integrated intensity was examined for different X-ray tube currents and fixed X-ray tube voltage of 40 kV and fixed meat thickness of 50 mm. The X-ray dose received by the scintillator decreased with decreasing the X-ray voltage. The intensity of the light emitted by the Cr: $\alpha\text{-Al}_2\text{O}_3$ ceramic was not much dependant on the value of the current and that of the Cr 0.1%:GGG crystal was detectably dependant on the value of the current. The Cr 0.1%:GGG crystal was used to evaluate the dose from the light yield under low dose X-ray irradiation.

The results of the studies reported are summarized as follows: (1) To establish the light yield measurements for the scintillators with infrared emission, the alpha-ray imaging method was applied to the light yield examination instead of general single photon counting method. (2): To perform systematic material research on the scintillators with infrared emission, Cr- or Ti-doped $(\text{Gd}_{1-y}\text{Y}_y)_3(\text{Ga}_{1-x}\text{Al}_x)_5\text{O}_{12}$ compounds were sintered and their properties were evaluated. (3): To understand the relationship between the light yield and its parameters in garnet-type oxide scintillators with infrared emission, the light yield, band gap and quantum yield of the Cr- or Ti-doped $(\text{Gd}_{1-y}\text{Y}_y)_3(\text{Ga}_{1-x}\text{Al}_x)_5\text{O}_{12}$ were evaluated. The light yield of the Cr-doped $(\text{Gd}_{1-y}\text{Y}_y)_3(\text{Ga}_{1-x}\text{Al}_x)_5\text{O}_{12}$ does not depend on only the band gap or the quantum yield. The light yield of the Ti-doped $(\text{Gd}_{1-y}\text{Y}_y)_3(\text{Ga}_{1-x}\text{Al}_x)_5\text{O}_{12}$ was low and undetectable. Cr 0.1%:GGG had highest light yield within Cr-doped oxide crystal scintillators with infrared emission. (4): To reveal the relationship between the emission wavelength and its parameters in the garnet-type oxide scintillators with infrared emission, the emission wavelength and lattice constants of the Ti-doped $(\text{Gd}_{1-y}\text{Y}_y)_3(\text{Ga}_{1-x}\text{Al}_x)_5\text{O}_{12}$ and alkaline earth metal substituted GGG were evaluated. Their emission peaks increased with increasing the lattice constant. (5): The Cr 0.1%:GGG crystal was used to perform the transmission experiment using the meat samples. The integrated intensity of the Cr 0.1%:GGG crystal was approximately 3.5 times greater than that of Cr: $\alpha\text{-Al}_2\text{O}_3$ ceramic and transmitted the meat sample with thickness up to 50 mm.