

Ion-Beam-Induced Luminescence Analysis of β -SiAlON:Eu Scintillator under Focused Microbeam Irradiation

Raj Kumar Parajuli,¹ Wataru Kada,^{1*} Shunsuke Kawabata,^{1,2} Yoshinori Matsubara,¹
Makoto Sakai,³ Kenta Miura,¹ Takahiro Satoh,² Masashi Koka,²
Naoto Yamada,² Tomihiro Kamiya,² and Osamu Hanaizumi¹

¹Graduate School of Science and Technology, Gunma University, 1-5-1 Tenjin cho Kiryu, Gunma 376-8515, Japan

²Takasaki Advanced Radiation Research Institute (TARRI), Japan Atomic Energy Agency (JAEA),
1233 Watanuki, Takasaki, Gunma 370-1292, Japan

³Graduate School of Medicine, Gunma University, 3-39-22 Showa-machi, Maebashi, Gunma 371-8511, Japan

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The scintillation properties and radiation durability of β -SiAlON:Eu were evaluated under focused microbeam irradiation conditions using 3 MeV protons. *In situ* observation of scintillation from β -SiAlON:Eu was monitored using ion-beam-induced luminescence (IBIL) and compared with that from ZnS:Ag scintillators. A comparison of the spectra of IBIL from both scintillators shows that the intensity of IBIL was analogous at different peak wavelengths of 545 nm for β -SiAlON:Eu and 450 nm for ZnS:Ag under the same irradiation conditions. Better radiation hardness towards focused proton microbeam irradiation was observed for the β -SiAlON:Eu scintillator when continuous measurements by IBIL were used. A decay constant of approximately 1.11×10^{16} , which is two orders of magnitude higher than that for ZnS:Ag, was obtained for the β -SiAlON:Eu scintillator for focused proton microbeam irradiation. IBIL was also capable of visualizing a previously damaged area of a ZnS:Ag scintillator, which corresponds to the focused beam scanning area of $100 \times 100 \mu\text{m}^2$. Meanwhile, the irradiated region was not significantly distinguishable from the nonirradiated region on the β -SiAlON:Eu scintillator under the same beam fluence. These results suggest that β -SiAlON:Eu could be an ideal candidate scintillator for convenient ionized particle beam monitoring and a diagnostic tool for focused and intense beam fluence conditions up to 10^{16} ions/cm².

1. Introduction

The radiation hardness of ionization particle detectors is a key issue for accelerator experiments, particularly for the utilization of focused ion microbeam probes for micrometer-sized material modifications^(1,2) or microanalysis.^(3,4) Irradiation by a focused microbeam significantly degraded the response of particle detectors because of its intense energy transfer to the detector body.^(5,6) Thus, scintillators are one of the candidates for a detector that can be conveniently renewed after irradiation.^(7,8) However, it is ideal to avoid significant degradation in the light emission from scintillators during measurement to maintain the accuracy of the measurement.⁽⁹⁾ For such a purpose, various types of scintillators have been evaluated for ionized radiation monitoring.⁽¹⁰⁾ Among the various scintillators,

*Corresponding author: e-mail: kada.wataru@gunma-u.ac.jp

silver-activated zinc sulfide (ZnS:Ag) is quite popular for convenient α -particle or ionized particle beam monitoring.^(11–13) The form of the powdered structure of ZnS:Ag is also beneficial for ionized particle detection because of its high sensitivity to primary particles distinct from the background.⁽¹⁴⁾ Much effort is continuously made in the development of various scintillators with properties superior to those of ZnS:Ag. However, the high availability and low cost of ZnS:Ag is an additional advantage, and it is still commonly used since it was first developed. However, sulfide-based phosphors have low chemical stability, causing their usefulness to depend on temperature and their degradation to occur because of radiation exposure. Therefore, it is necessary to find alternative candidates for scintillators for intense ion beam irradiation with performance comparable or superior to that of ZnS:Ag.

On the other hand, there is growing interest in high-luminescent-yield light conversion substrates for multiphosphor-converted white-light-emitting diodes (LEDs).⁽¹⁵⁾ Among candidate substrates, β -SiAlON:Eu ceramics are phosphors with excellent luminescence properties and outstanding thermal and chemical stability⁽¹⁶⁾ because of their hexagonal crystal structure equivalent to that of substituted β -phase silicon nitride (β -Si₃N₄) ceramics.⁽¹⁷⁾ Low thermal quenching would be delivered by doping with europium (Eu), and the luminescence properties of the phosphor are maintained at even high temperatures of approximately 150 °C.⁽¹⁸⁾ Because of its high efficiency and crystal structure, β -SiAlON:Eu is expected to be a successful candidate as an alternative scintillator to ZnS:Ag for the convenient beam monitoring of intense ionized beam irradiation. Since the powders are originally fabricated for mass production, β -SiAlON:Eu is very promising because of its wide availability at a reasonable cost if its basic properties as a scintillator could be established by comparing its operation with conventionally available scintillators.

In this study, ion-beam-induced scintillation and the radiation hardness of β -SiAlON:Eu were preliminarily evaluated under focused proton microbeam irradiation conditions. To obtain the luminescence spectrum of a β -SiAlON:Eu scintillator, an ion-beam-induced luminescence (IBIL) analysis system using a focused proton microbeam was employed. The IBIL system was developed on the same microbeam line as a proton beam writing (PBW) system, which is capable of irradiating a target with any desired two dimensional patterns. The powders of β -SiAlON:Eu originally designed as the substrate of LEDs were processed to be fixed on the irradiation. Under focused proton beam irradiation conditions, the scintillation response was observed and compared with that of a commercially available ZnS:Ag scintillator. IBIL was continuously monitored from both β -SiAlON:Eu and ZnS:Ag scintillators to obtain the relative radiation tolerability with a beam fluence up to 10¹⁶ ions/cm². The results obtained in this study suggested that β -SiAlON:Eu was capable of being used as a beam-monitoring tool for focused microbeam irradiation conditions, and it was more durable in higher beam fluence than the conventional standard ZnS:Ag scintillator.

2. Materials and Methods

2.1 Preparation of IBIL target of β -SiAlON:Eu

A focused proton microbeam irradiation experiment on β -SiAlON:Eu was performed on a microbeam line of the 3 MV single-ended accelerator at Takasaki Advanced Radiation Research Institute (TARRI), Japan Atomic Energy Agency (JAEA).⁽¹⁹⁾ The sample was prepared on a sample holder used in in-air particle-induced X-ray emission (PIXE) analysis.⁽²⁰⁾ A powdered sample of β -SiAlON:Eu (DENKA GR-200) with a mean particle diameter of 21 μm ⁽¹⁶⁾ was employed for the

irradiation. β -SiAlON:Eu powders were mixed with water and then homogeneously spread on a polyimide film at a thickness of approximately $7\ \mu\text{m}$.⁽²⁰⁾ This film was attached to the sample holder for PIXE analysis and also worked as a beam extraction window for the external proton beam irradiation. To exclude the effect of auto-fluorescence from the polyimide film, another sample holder of aluminum plate was also used for the irradiation. Under both conditions, the water was removed by drying at room temperature (RT) for 10 min. This procedure allowed us to fix the scintillator without any adhesives between the sample holders and the scintillators.

2.2 IBIL analysis

Figure 1 shows the analysis system for IBIL, which consists of simple microoptics.⁽²¹⁾ A focused proton microbeam with energy up to 3 MeV was employed for IBIL measurements on the SiAlON scintillator in conjunction with the micrometer-scale patterned irradiation technique of a PBW system.⁽²²⁾ The scanning pattern of the proton microbeam was controlled by electrostatic X - Y scanners. The PBW system was capable of irradiating the sample with desired two-dimensional patterns over a maximum scanning area of $800 \times 800\ \mu\text{m}^2$.⁽²³⁾ Since the IBIL optics shared its focal point with that of the proton microbeam, IBIL from the irradiated area was collected separately from the background from visible lights in the environment with a high signal-to-noise (S/N) ratio.⁽²⁴⁾ IBIL spectroscopy was performed using an electrically cooled back-thinned charge-coupled device (CCD) spectrometer (Solid Lambda CCD, Spectra Co., Ltd.) with an effective wavelength from 200 to 980 nm.⁽²⁵⁾ Continuous IBIL measurement was achieved by repeatedly acquiring spectra at a high rate with a minimum measurement time of 19 ms. Although the CCD spectrometer cannot obtain the absolute emission rate of IBIL photons, changes in the chemical composition of the target appear as changes in the structure of the IBIL spectrum.⁽²⁶⁾ For comparison of IBIL intensity changes and IBIL imaging, the spatial resolution is assumed to correspond to the typical diameter of the focused microbeam (approximately $1\ \mu\text{m}$),⁽²⁷⁾ which was evaluated from the secondary microscopic image of the copper grid for transmission electron microscope (TEM) application.⁽²⁸⁾

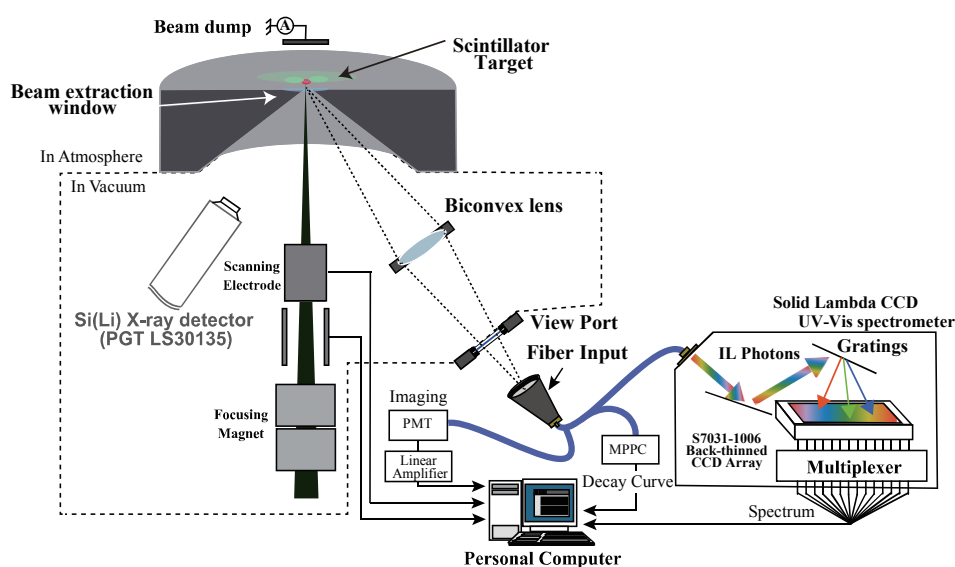


Fig. 1. (Color online) Schematic of experimental setup of IBIL analysis system for the evaluation of radiation hardness of a β -SiAlON:Eu scintillator.

Since the spectrometer is not sensitive to the individual IBIL incident photons, it could be replaced by a photon-counting-mode photomultiplier (PMT, Hamamatsu Photonics; H10682-210) and a Geiger-mode avalanche photodiode (APD)-based multipixel photon counter (MPPC, Hamamatsu Photonics C10507-11-100U) for photon counting of the IBIL. Among the detectors used in this experiment, MPPC had the fastest response; therefore, the degradation of IBIL could be visualized with this detector, while PMT had the highest sensitivity to individual IBIL photons. Also, IBIL imaging was accomplished with the photon counting mode PMT to visualize the degraded region with the highest contrast within this experimental setup.

3. Results and Discussion

3.1 Comparison of IBIL spectra of ZnS:Ag and β -SiAlON:Eu

The IBIL spectra of (a) ZnS:Ag and (b) β -SiAlON:Eu induced by focused 3 MeV proton microbeam were obtained individually and reported as shown in Fig. 2. The IBIL was excited by protons with a variable beam current of approximately 1 pA. A CCD-based spectrometer was employed for the comparison of the spectra at the beginning of the irradiation. The intensity of the IBIL was similar for the two scintillators, with different peak wavelengths for β -SiAlON:Eu and ZnS:Ag exhibiting a broad band structure. The peak at around 545 nm was obtained for β -SiAlON:Eu, which was longer than that of ZnS:Ag (450 nm) under the same irradiation conditions. The peak wavelength and structure of the IBIL spectrum of β -SiAlON:Eu were similar to those of the cathodoluminescence spectrum of β -SiAlON:Eu.⁽²⁹⁾ The similar intensities of IBIL from both thin-layered scintillators suggest that the β -SiAlON:Eu scintillator has a comparable light emission yield to that of the ZnS:Ag, although the absolute scintillation efficiency could not be evaluated from the configuration of the microoptics. Both IBILs had a similar full width at half maximum (FWHM) of approximately 45 nm. It is also remarkable that there are small differences in the peak wavelength, which could also be an advantage of β -SiAlON:Eu, because most photon detectors have maximum quantum efficiency at wavelengths at or above 500 nm.⁽³⁰⁾

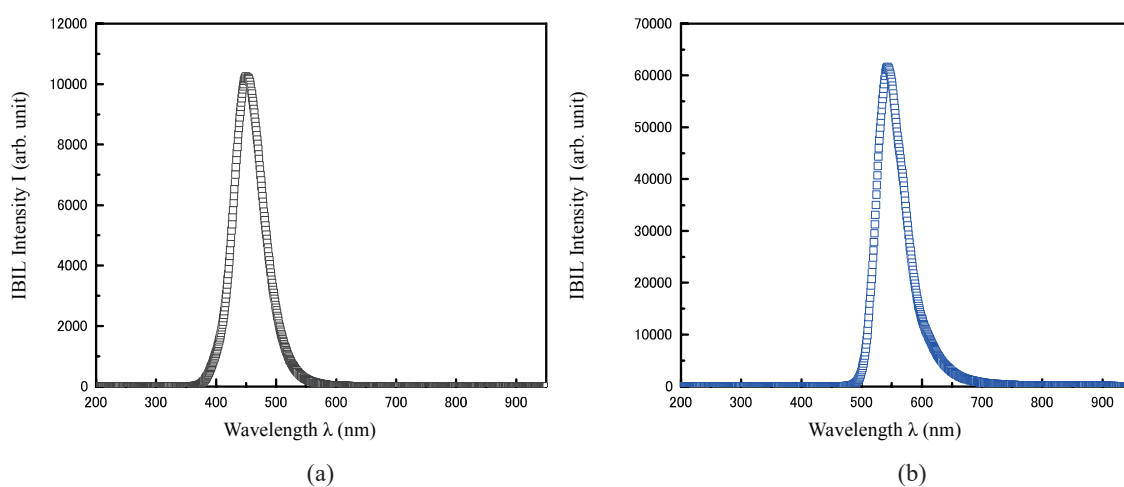


Fig. 2. (Color online) IBIL spectra obtained for (a) ZnS:Ag and (b) β -SiAlON:Eu excited by 3 MeV proton beam irradiation. A peak at approximately 450 nm was obtained for IBIL from ZnS:Ag and one at approximately 545 nm for IBIL for β -SiAlON:Eu.

3.2 Continuous IBIL monitoring

As irradiation continued, the structure of the IBIL spectrum of ZnS:Ag rapidly degraded, while the IBIL of β -SiAlON:Eu showed little fluctuation without significant degradation. Since the spectrometer is not sensitive to individual incident photons, the photodetectors of MPPC H10682-210 were employed to compare IBIL intensity changes during focused microbeam exposure. The radiation resistivity of both scintillators is compared in Fig. 3 as the decay trend of IBIL for ZnS:Ag and β -SiAlON:Eu with respect to beam fluence and IBIL counts. A model using two decay factors (F_1 and F_2) as expressed in Eq. (1) was employed to fit the IBIL intensity $I(F)$ (arb. unit) as a function of the beam fluence F (ions/cm²), where a constant factor I_0 was also included to express the baseline of the background and a slow decay component.

$$I(F) = I_0 + I_1 \times \exp[-(F - F_0)/F_1] + I_2 \times \exp[-(F - F_0)/F_2] \quad (1)$$

A steep decay was observed for ZnS:Ag, whereas almost constant radiation tolerability was observed for the β -SiAlON:Eu scintillator. This fact was also cross-checked using the decay factors (F_1 and F_2), which were determined for ZnS:Ag ($F_1 = 2.74 \times 10^{14}$ and $F_2 = 4.18 \times 10^{15}$) and β -SiAlON:Eu (F_1 and $F_2 = 1.11 \times 10^{16}$) from the fitting. The differences in the magnitudes of the decay factors correspond to the differences in the degradation of the IBIL responses of the two scintillators. The difference in the degradation of IBIL corresponds to the structural changes in the host crystal of the scintillator during ion bombardment. It appears that IBIL from ZnS:Ag and β -SiAlON:Eu showed fluctuation according to the fluctuation of the position and the current of the proton microbeam during the measurement. This experimental result suggests that the β -SiAlON:Eu scintillator has a better tolerance to radiation of the proton microbeam without any distortion caused by ion impact.

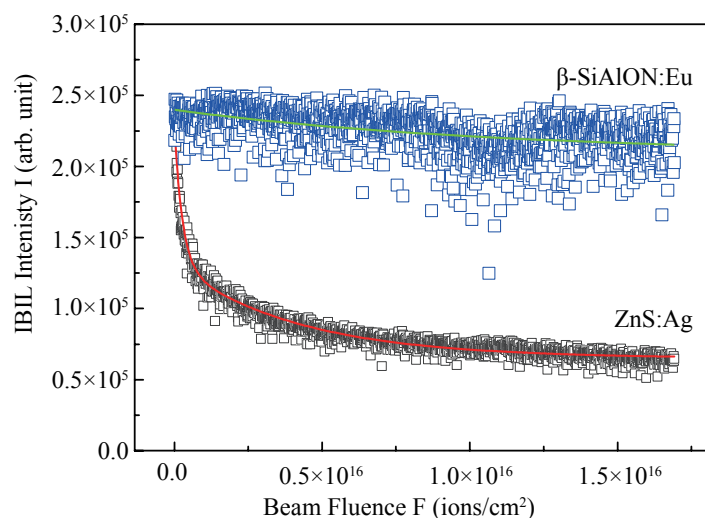


Fig. 3. (Color online) Comparison of decay scheme of IBIL for ZnS:Ag and β -SiAlON:Eu scintillator under intense fluence up to 1.5×10^{16} ions/cm².

3.3 *In situ* analysis by IBIL imaging

After the intense irradiation of the 3 MeV proton microbeam, *in situ* imaging of IBIL was performed using the same beam probe and photon-counting signals of H10682-210 PMT. Figure 4 shows comparisons of two-dimensional IBIL images for ZnS:Ag and β -SiAlON:Eu scintillator targets before and after irradiation. In each image, the irradiated area of $100 \times 100 \mu\text{m}^2$ size was indicated for a maximum scanning area of $200 \times 200 \mu\text{m}^2$. Intense beam irradiation ($100 \times 100 \mu\text{m}^2$) was applied with a beam current of 100 pA for approximately 60 min, and IBIL imaging was carried out with less than 1 pA. Only a few raster scans were carried out on the scintillators to avoid additional damage caused by IBIL imaging. IBIL was almost eliminated in the irradiated area on the ZnS:Ag scintillator as seen in the comparison of images before and after irradiation. In contrast, the region cannot clearly be recognized in the comparison of two IBIL images for the β -SiAlON:Eu scintillator target. This result shows the usefulness of the β -SiAlON:Eu scintillator as a convenient particle detection material under beam irradiation conditions.

Since the β -SiAlON:Eu scintillator showed little degradation under continuous IBIL measurement, additional experiments on IBIL imaging for single particles of the β -SiAlON:Eu scintillator were carried out, as shown in Fig. 5, to evaluate the sustainability and uniformity of the IBIL from a single particulate target. The scanning beam of the proton microbeam has a scanning speed of several microseconds/pixel with a raster scan. Since there are no horizontal stripes on the IBIL image, IBIL induced by proton impact would have a decay time of less than several microseconds, which corresponded to the time spent scanning on the single point. During the

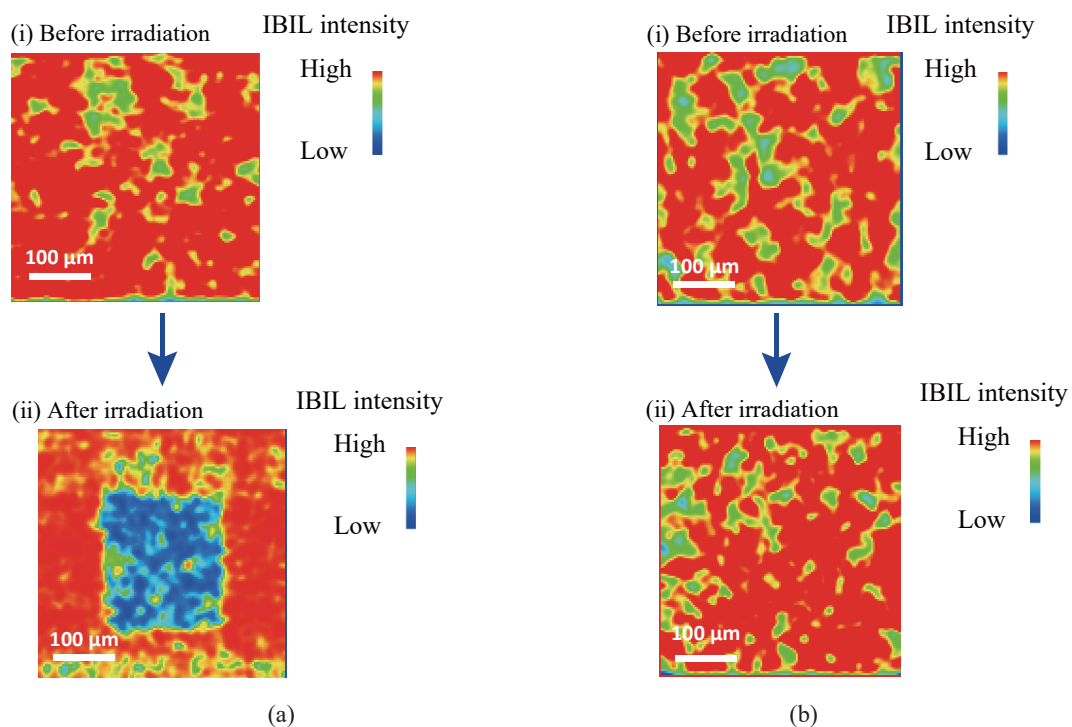


Fig. 4. (Color online) IBIL imaging for (a) ZnS:Ag scintillator and (b) β -SiAlON:Eu scintillator. For both scintillators, IBIL images (i) before and (ii) after irradiation (intense irradiation area of $100 \times 100 \mu\text{m}^2$) were visualized in IBIL images of the entire scanning area of $200 \times 200 \mu\text{m}^2$.

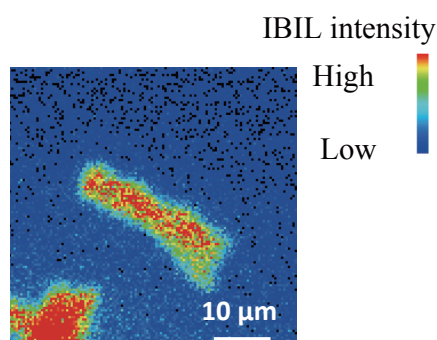


Fig. 5. (Color online) IBIL imaging for a single particle of the β -SiAlON:Eu scintillator.

irradiation, there are few fluctuations in IBIL intensity. Moreover, a uniform distribution of IBIL in the entire β -SiAlON:Eu particle was observed. These results suggest that the β -SiAlON:Eu scintillator may be applicable as a fluorescence staining material for a charged-particle microscope using electron, proton, or heavier particles, i.e., ion-photon emission microscopy (IPEM),⁽³¹⁾ where scintillators with high radiation hardness are required.

4. Conclusions

The scintillator properties and radiation resistance of β -SiAlON:Eu were preliminarily evaluated using a focused proton microbeam. IBIL spectra and quantitative measurements of IBIL intensity were collected for β -SiAlON:Eu and compared with ZnS:Ag under intense proton irradiation. Comparison of IBILs revealed that similar light emission yields were obtained for ZnS:Ag and β -SiAlON:Eu. Continuous observation of IBIL during intense proton irradiation revealed that the β -SiAlON:Eu scintillator has better radiation resistivity than the conventional standard of an ZnS:Ag scintillator. Postimaging of IBIL around the proton bombardment region suggested that the β -SiAlON:Eu scintillator is sustainable under harsh and intense ion beam irradiation conditions. Accurate measurement of the temperature dependence of IBIL for β -SiAlON:Eu is desirable to determine the threshold of the operational temperature range of this scintillator.

The remarkable properties of β -SiAlON:Eu suggest that it could be a successful candidate as a beam-monitoring tool for focused proton microbeams. Furthermore, single-particle imaging of β -SiAlON:Eu was also successfully demonstrated with IBIL imaging. Since little degradation was observed during irradiation, β -SiAlON:Eu scintillators are capable of being used as a fluorescence staining medium for an ion microscope if the mean diameter of the scintillator could be optimized. It is necessary to obtain the IBIL response of β -SiAlON:Eu at high temperatures to determine its thermal response as a radiation detector.

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